RECOVERY OF BIO-FUELS FROM AGRICULTURAL RESIDUES

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by

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CERTIFICATE

This is to certify that the thesis entitled **"Recovery of bio-fuels from agricultural residues"** by **Mr. Vikranth Volli** submitted to the National Institute of Technology, Rourkela for the Degree of Master of Technology is a record of bonafide work, carried out by him in the Department of Chemical Engineering under my supervision. I believe that the thesis fulfils part of the requirements for the award of master of Technology. The results embodied in the thesis have not been submitted for the award of any other degree.

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ABSTRACT

De-oiled cakes, a source of biomass in the form of agriculture residue, could be an ideal source for the production of bio fuels that can be used as a substitute for the existing conventional fossil fuels which are at the verge of getting extinct. Though there are many biomass conversion processes like pyrolysis, combustion, gasification, liquefaction, hydrogenation, pyrolysis has gained special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen. In this study, neem, mustard and mahua de-oiled cakes were pyrolysed at a temperature of 300 ^{0}C to 700 ^{0}C at a heating rate of 25 ^{0}C /min. The maximum liquid yield obtained was 40.23% at a pyrolysis temperature of 400 ^{0}C for neem cake, 53.26% at a pyrolysis temperature of 550 ^{0}C for mustard cake and 41.2 % at a pyrolysis temperature of 550 ^{0}C for mahua cake. The effect of temperature on pyrolysis of liquid product, char, gaseous product and reaction time were studied. The various characteristics of liquid product obtained were identified on the basis of standard test methods. Effect of heating rate on the mass loss for all the raw materials were examined using the thermo gravimetric analysis profiles (TGA). The empirical formulas of the bio-oil with heating value were established. The chemical compositions of the bio-oils and char were investigated using FTIR, SEM, EDX and GC-MS. Further structural analysis of pyrolysis oil was conducted using 1H-NMR spectroscopy. The fuel properties of the bio-oil such as kinematic viscosity, flash point, fire point, cloud point, pour point and specific gravity were also determined. Engine performance, combustion and emission characteristics of blends of mustard cake pyrolytic oil with diesel (10%, 20%, 30%, 40%, 50%) were also studied. The chemical characterization and engine performance showed that bio-diesel of 30% blend can be substituted with diesel fuel and the bio-oil obtained from these raw materials may be potentially valuable as chemical feedstock.

Keywords: De-oiled cakes, neem cake, mustard cake, mahua cake, pyrolysis, bio-oil, TGA, FTIR, SEM, EDX, GC-MS, 1 H-NMR and Engine Performance.

RECOVERY OF BIO-FUELS FROM AGRICULTURAL RESIDUES

CHAPTER - 1

INTRODUCTION

INTRODUCTION

The life of convectional fossil fuels has become limited in the present era, where the use of energy and their source has been growing faster than the world population. It is expected that the world population would increase by 0.9 percent per year, from 6498 million in 2005 to 8469 millions in 2035. Indian population will increase from 1165 million to 1528 million from the year 2007 to 2035. The annual average percent change from 2007 to 2035 will be around 1 % in India. Table. 1 shows world population by region. Along with increase in population, the energy needs are also increasing. The world energy consumption would increase by 49 percent, or 1.4 percent per year, from 495 quadrillion Btu in 2007 to 739 quadrillion Btu in 2035[1].

On the global scale, increase in the emissions rates of greenhouse gases produced from the use of these conventional fossil fuels presents a threat to the world climate**.** The major exhaust emissions that contribute to pollution and global warming are SO_2 and CO_2. World carbon dioxide emissions grow from 29.7 billion metric tons in 2007 to 33.8 billion metric tons in 2020 and 42.4 billion metric tons in 2035 and in India it is expected to increase by 1.8 per year from 314 million metric tons in 2005 to 606 million metric tons in 2035[1]. Same trends are expected for SO_2 emissions. In the year 2000 the SO_2 levels in India was about 7919.6 thousand metric tons and it is expected increase further [2].

The major sources of this energy include liquid fuel, natural gas, coal and electricity. Table 2, 3 shows the statistical data of worlds total primary energy consumption by region and worlds total energy consumption by fuel. Conventional liquid fuels are the major contributor for these energy sources and if these are used extensively, they might get extinct. With declining fossil fuel resources and increased demand for their products, there is an urgent need to develop economical, environment friendly, energy-efficient processes and resources for the production of fuels and chemicals.

Biomass, which contributes to one-seventh of the world-wide energy consumption and for as much as 43% of the energy consumption in some developing countries, has a great potential to be a renewable source and can be replaced with the conventional fossil fuels [3]. Though there are many biomass conversion processes like pyrolysis, combustion, gasification, liquefaction, hydrogenation, pyrolysis has gained special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen**.**

The liquid product obtained by the pyrolysis of biomass may also be upgraded to refined fuels, added to petroleum refinery feedstock or may contain chemicals in economical recoverable concentrations [4].

Table. 1 World population by region (millions)

Region/ country	History			Projections					Average annual percent change, 2007-2035
	2005	2006	2007	2015	2020	2030	2035		
OECD (Organization for Economic Cooperation and Development)									
OECD North America	432	436	441	477	500	523	546	569	0.9
United state	297	300	302	327	327	343	359	391	0.9
Canada	32	33	33	36	38	40	42	43	1.0
Mexico	103	104	105	114	120	125	130	135	0.9
OECD Europe	535	538	541	558	565	571	575	577	0.2
OECD Asia	200	200	201	203	202	201	199	196	-0.1
Japan	128	128	128	126	124	122	119	116	-0.3
South Korea	48	48	48	49	49	49	49	48	0.0
Australia/New Zealand	25	25	25	27	28	30	31	32	0.8
Total OECD	**1,167**	**1,175**	**1,183**	**1,238**	**1,267**	**1,294**	**1,319**	**1,342**	**0.5**
Non-OECD									
Europe and Russia.	341	341	340	338	336	333	329	324	-0.2
Russia	143	143	142	138	135	132	129	125	-0.4
Other	198	198	198	200	200	201	200	198	0.0
Non-OECD Asia	3,446	3,486	3,525	3,841	4,021	4,175	4,299	4,398	0.8
China	1,308	1,314	1,321	1,386	1,421	1,443	1,452	1,452	0.3
India	1,131	1,148	1,165	1,294	1,367	1,431	1,485	1,528	1.0
Other Non -OECD Asia	1,008	1,024	1,039	1,160	1,233	1,300	1,363	1,418	1.1
Middle East	191	195	199	231	251	270	288	305	1.5
Africa	902	919	939	1,098	1,197	1,297	1,395	1,494	1.7
Central and South America	451	458	464	511	538	563	586	511	1.0
Brazil	187	190	192	210	220	229	236	243	0.8
Other Central and South America	265	268	272	301	318	334	349	363	1.0
Total Non-OECD	**5,332**	**5,398**	**5,467**	**6,018**	**6,343**	**6,638**	**6,897**	**7,127**	**1.0**
Total World	**6,498**	**6,573**	**6,650**	**7,256**	**7,610**	**7,932**	**8,217**	**8,469**	**0.9**

Biodiesel, chemically called methyl or ethyl esters are renewable fuels produced from biomass, vegetable oil and animal fat through a chemical process. Vegetable oils are highly viscous because of their higher molecular mass. This makes them unfit for usage directly in diesel engines. Utilizing biodiesel in diesel engines with slight modifications has proven to be more advantageous because of its reduction in pollution levels. It is estimated that India will be able to produce 288 metric tones of biodiesel by the end of 2012, which will supplement 41.14% of the total demand of diesel fuel consumption in India [5].

Table. 2 World total primary energy consumption by region, 2005-2035 (Quadrillion Btu)

Region/ Country	History			Projections					Average annual percent change, 2007-2035
	2005	2006	2007	2015	2020	2030	2035	2005	
OECD (Organization for Economic Cooperation and Development)									
OECD North America	122.4	121.8	12.7	124.3	129.4	134.9	140.2	146.3	0.6
United state	100.5	99.8	101.7	101.6	105.0	108.3	111.2	114.5	0.4
Canada	14.8	14.5	14.3	14.6	15.4	16.3	17.2	18.2	0.9
Mexico	7.1	7.4	7.7	8.1	9.0	10.4	11.8	13.5	2
OECD Europe	82.4	82.9	82.3	82.0	83.0	85.0	86.5	88.2	0.2
OECD Asia	39.0	39.5	39.7	39.7	41.8	43.3	44.8	46.3	0.5
Japan	23.1	23.3	22.8	21.1	21.9	22.1	22.1	22.2	-0.1
Australia/New Zealand	6.6	6.7	7.2	8	8.2	8.5	8.9	9.2	0.9
Total OECD	**24.38**	**244.1**	**245.7**	**246.0**	**254.2**	**263.2**	**271.4**	**280.7**	**0.5**
Non-OECD									
Europe and Russia.	50.4	51	51.5	52.4	54.2	56.2	57.8	60.2	0.6
Russia	29.7	30.5	30.5	30.7	31.6	32.8	33.9	35.5	0.5
Other	20.7	20.6	21	21.7	22.5	23.3	23.9	24.7	0.6
Non-OECD Asia	112.6	119.8	127.1	159.3	187.8	217	246.9	277.3	2.8
China	68.4	73	78	101.4	121.4	142.4	162.7	181.9	3.1
India	17.5	18.8	20.3	24.3	28.2	31.1	34.1	37.6	2.2
Other Non -OECD Asia	26.7	27.8	28.8	33.7	38.2	43.5	50.2	57.8	2.5
Middle East	22.8	23.9	25.1	32.9	36.5	39.1	41.8	45.7	2.2
Africa	17.2	17.3	17.8	20.8	22.5	24.6	26.5	29.0	1.8
Central and South America	26	27.1	28	32.1	35.5	38.7	42.2	45.7	1.8
Total Non-OECD	**229.0**	**239**	**249.5**	**297.5**	**336.3**	**375.5**	**415.2**	**458.0**	**2.2**
Total World	**472.7**	**483.1**	**495.2**	**543.5**	**590.5**	**638.7**	**686.5**	**738.7**	**1.4**

But prices of biodiesel are little high when compared to petro-diesel due to the higher cost of raw material and it reduces the availability of vegetable oils. As the demand for edible oils for food has increased tremendously in recent years, large-scale production of bio diesel from edible may cause negative impact leading to economic imbalance.

Table.3 World total energy consumption by fuel, 2005-2035 (Quadrillion Btu)

Fuel	History			Projections					Average annual percent change, 2007-2035
	2005	2006	2007	2015	2020	2030	2035	2005	
Total World									
Liquids	170.4	172.8	174.7	179.3	186.0	197.2	210	223.6	0.9
Natural Gas	106.3	108.3	112.1	129.1	141.2	150.2	155.8	162.0	1.3
Coal	122.3	126.4	132.4	139.1	152.4	167.8	185.6	206.3	1.6
Nuclear	27.5	27.8	27.1	32.3	37.4	41.1	43.9	47.1	2
Others	46.2	47.9	48.8	63.8	73.4	82.4	91.2	99.8	2.6
Total	**472.7**	**483.1**	**495.2**	**543.5**	**590.5**	**638.7**	**686.5**	**738.7**	**1.4**

This has become the primary objective, to find raw materials that are cheaper than vegetable oils. Wastes can be one such source. Now a days, most of the research is focused on using these wastes to produce value added fuels and chemical. India is an agricultural country and a store house of many oil seeds. Table.4 shows the production details of the oil seeds in India. Oil is extracted from these seeds my mechanical pressing and on an average these seeds contain 30-40% of oil. The left over is residue and is an ideal source for extraction of bio-fuels.

Research Objective:

The main objective of the present work is to study how de-oiled cakes in the form of agricultural residue can be a potential source in the production of bio-fuels. In the present investigation three de-oiled cakes namely mustard de-oiled cake, neem de-oiled cake, mahua de-oiled cake were pyrolysed in a semi batch reactor to determine the optimum conditions for the production of bio-oil. The effect of temperature on yields of liquid product, char, gaseous products and reaction time were studied.

The bio-oil obtained was characterized for it fuel properties and composition by 1H-NMR, FTIR, GC/MS and CHNS. Physical properties of the bio-oil such as kinematic viscosity, flash point, fire point, cloud point, pour point and specific gravity were also determined. Effect of heating rate on the mass loss for all the raw materials was examined using the thermo gravimetric analysis profiles (TGA). Calorific values and empherical formula of the bio-oil and char were established. Char obtained was characterized for its composition by SEM-EDX and CHNS analysis. BET Surface area of the char was also determined to find out whether it can be used as an adsorbent.

The bio-oil thus obtained from mustard de-oiled cakes was blended with diesel in various proportions (10%, 20%, 30%, 40% and 50%) and diesel engine was run by using these blends to evaluate the performance and emission characteristics. Engine tests was carried out for analyzing performance characteristics such as break thermal efficiency (BTE), specific fuel consumption (SFC), exhaust gas temperatures (EGT) and emission levels of CO, CO_2, HC and NOx were also measured from the exhaust gases.

Table. 4 India oil seed production

Oil-seeds	Oil content	Production (Million tons)				
		2009-10	2008-09	2007-08	2006-07	2005-06
Ground nut	35-40	5.12	5.92	6.89	5.35	6.25
Castor seed	45-50	0.93	0.98	0.91	00.78	0.91
Sesame seed	48-49	0.76	0.58	0.66	0.61	0.60
Mustard	42-45	6.32	6.20	4.59	6.02	6.77
Linseed	35-45	0.16	0.13	0.18	0.19	0.20
Niger seed	32-43	0.08	0.08	0.07	0.07	0.11
Safflower	30-45	0.15	0.17	0.17	0.19	0.21
Sunflower	39-49	0.99	1.15	1.46	1.60	1.62
Soybean	20-30	8.50	8.90	9.46	7.96	7.05
Neem	20-30	0.16	--	--	--	--
Mahua	33-40	0.18	--	--	--	--

CHAPTER - 2
LITERATURE REVIEW

2.1 BIOMASS:

Biomass is name given to anything that is living on earth surface. These are substances that use solar energy for their survival. Plants use the process of photosynthesis for the production of biomass. It is a general term used to produce all biologically produced matter. Biomass is one of the most important potential and the only carbon-containing renewable energy resources. Biomass mainly consists of cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars and starches and among these compounds, cellulose, hemicelluloses, and lignin are the three main constituents. Table.5 gives the typical levels of cellulose, hemicelluloses, and lignin [6].

Table. 5 Typical levels of cellulose, hemicelluloses and lignin in biomass

Component	Percent Dry weight	Description
Cellulose	40–60	A high-molecular-weight (106 or more) linear chain of glucose linked by b-glycosidic linkage. This chain is stable and resistant to chemical attack
Hemicelluloses	20–40	Consists of short, highly branched chains of sugars (five-carbon sugars such as D-xylose and L-arabinose, and six-carbon sugars such as D-galactose, D-glucose, and D-mannose) and uronic acid. Lower molecular weight than cellulose. Relatively easy to be hydrolyzed into basic sugars
Lignin	10–25	A biopolymer rich in three-dimensional, highly branched polyphenolic constituents that provide structural integrity to plants. Amorphous with no exact structure. More difficult to be dehydrated than cellulose and hemicelluloses

2.2 WHY BIOMASS ?[7]

1. Biomass is renewable and available essentially for all countries in the world and at anytime (thus of a high energy security).
2. High availability of the resource.
3. Great variety of biomass types and possible energy uses.
4. Biomass contains negligible sulfur, nitrogen and metal contents hence it helps in

minimizing the acid rain.

5. It can help mitigate climate change, water pollution and soil erosion.
6. Valuation of wastes.
7. Fixation of rural population and depletion of fossil fuels.
8. Usage of biomass does not result in a net increase in the CO_2 concentration in the atmosphere because the carbon released during combustion was taken recently from the atmosphere by photosynthesis during biomass growth.

2.3 SOURCES OF BIOMASS:

The major sources of biomass resource include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae. Biomass resources are categorized into three types [8]. They are

Wastes: Agricultural production wastes, agricultural processing wastes, crop residues, mill wood wastes, urban wood-wastes, and urban organic wastes.

Forest Products: Wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc., from forest clearings.

Energy Crops: Short rotation woody crops, herbaceous woody crops, grasses, starch crops (corn, wheat and barley), sugar crops (cane and beet), oilseed crops (soya bean, sunflower, safflower).

2.4 BIOMASS CONVERSION PROCESSES:

The energy form biomass can be converted to useful forms by using a number of different processes [9]. Factors that influence the choice of conversion process are:

Type and quantity of biomass feedstock

- Desired form of the energy i.e. end-use requirements
- Environmental standards
- Economic conditions;
- Project specific factors

In many situations it is the form in which the energy is required that determines the process route followed by the available types and quantities of biomass [9]. Broadly they are classified into two types. Figure. 1 shows the block diagram of various conversion process and uses of their products.

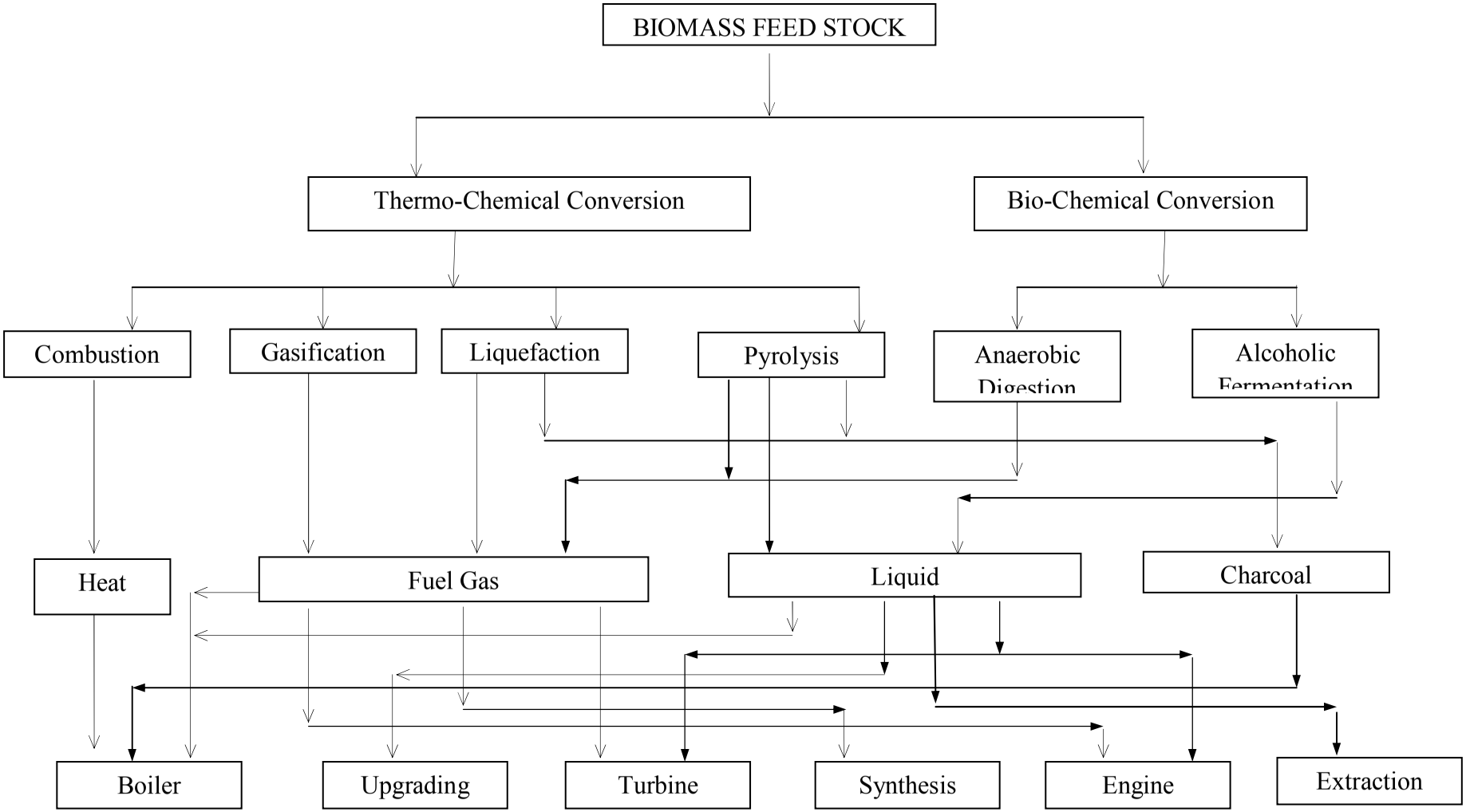

Figure. 1 Block diagram of various conversion process and uses of their products.

They are

1. Thermo chemical processes
2. Bio-chemical processes

Thermo-chemical conversion is classified into four processes. They are

1. Combustion
2. Gasification
3. Liquefaction
4. Pyrolysis

2.4.1 COMBUSTION:

Combustion is an exothermic chemical reaction accompanied by large heat generation and luminescence. In this process biomass is directly burnt in the presence of air to convert chemical energy into heat, mechanical power, or electricity, etc. Combustion proceeds by gas phase reaction, surface reaction or both following processes such as fusion, evaporation, mixture, diffuse, convection, heat conduction, radiation complexly at high velocity. It is possible to burn any type of biomass but in practice combustion is feasible only for biomass with moisture content less than 50%. Combustion of biomass produces hot gases at temperatures around 800 - 1000 ^{0}C that can directly be used for the production of electricity [10]. Wood or woody biomass burns to carbon dioxide (CO_2) and water vapor (H_2O) as follows

$$C_{42}H_{60}O_{28} + 43O_2 \longrightarrow 42CO_2 + 30H_2O$$

Many countries are using biomass by burning it as fuel to generate heat. According to a general rule, though complete combustion is impossible, combustion requires the three T's, meaning sufficiently high temperature, strong turbulence of the air as mixture, and a long residence time of the mixture in the fire chamber [10]. Turbulence and long residence time bring each pyrolysis-gas molecule close to oxygen and provide chances for more combustion. This combustion proceeds in many intermediate steps and with the various wood pyrolysis products on different routes.

2.4.2 GASIFICATION:

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range 800 – 900 ^{0}C. Air gasification is the most widely used technology since a single product is formed at high efficiency. and without requiring oxygen. Either air, oxygen enriched air or oxygen may be used with steam added as a reagent and/or temperature control medium. Raw materials are mainly wood chips and corn stalks. The low calorific value (CV) gas produced (about 4–6 MJ/Nm^3) can be burnt directly or used as a fuel for gas engines and gas turbines[8]. The product gas can be used as a feedstock (syngas) in the production of chemicals (e.g. ethanol). The biomass is heated in insufficient supply of air. The reactions are as follows

$C + O_2 \longrightarrow CO_2$

$C + ½\ O_2 \longrightarrow CO$

$CO + ½\ O_2 \longrightarrow CO_2$

$CO2 + C \longleftrightarrow CO_2$

Methane and hydrogen are also formed simultaneously by thermal splitting of organic material.

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

In recent years, many attempts have been made to gasify cellulosic materials, such as cotton, wood, bark, peat and rice hulls [8]. One promising concept is the biomass integrated gasification/combined cycle, where gas turbines convert the gaseous fuel to electricity with a high overall conversion efficiency.

2.4.3 LIQUEFACTION:

Liquefaction process converts biomass into liquid oils, hydrogen, bio fuels, synthesis gas, bio chemicals and alcohols. Liquefaction process can treat high moisture content biomass. Liquefaction can be accomplished directly or indirectly.

Direct liquefaction, is a low-temperature and high pressure process in which biomass is broken down into fragments of small molecules in water or another suitable solvent. Lignocelluloses biomass materials are the most widely used types of biomass for bio-oil production through

liquefaction. In liquefaction process, biomass undergoes depolymerization and is decomposed into monomer units. These monomer units, however, may be re-polymerized or condensed into solid chars, which are undesirable [6,7]. A solvent is generally added to slow down the higher order solid-state reactions, thus reducing the detrimental condensation reactions. The use of catalysts is a critical factor in biomass liquefaction as it can reduce the required reaction temperature, enhance reaction kinetics, and improve the yield of desired products.

Indirect liquefaction of biomass is accomplished by first gasifying it to produce a synthesis gas consisting of hydrogen and oxides of carbon, which in turn are converted to any one of a number of liquid fuels and chemicals by suitable choice of catalyst, synthesis gas composition and reaction conditions. This approach to producing synthesis fuels and chemicals has been extensively investigated that the carbonaceous feed material, but less for biomass or other feedstocks.

2.4.4 PYROLYSIS:

Amongst the thermo-chemical processes, pyrolysis has received increasing attention because they produce high energy pyrolytic oils in addition to char and gas. Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into solid charcoal, liquid (bio-oil), and gases at higher temperatures. Pyrolysis processes are of three types. They are

1. Slow or Conventional pyrolysis
2. Fast Pyrolysis
3. Flash Pyrolysis

Conventional or slow pyrolysis process, are done at relatively long vapor residence time (minutes to days), at low heating rate (3- 5 C/min) and moderate temperatures of around 300 - 400 ^{0}C. This process is mostly used to maximize char yield which increases up to 30% when compared to other processes.

Fast pyrolysis is a pyrolysis process occurring at high heating rate (as high as 50 - 100 ^{0}C/min), short residence time (minutes to seconds) and higher temperatures of around 450- 600 ^{0}C. It particularly favors the formation of liquid products, but inhibits the formation of solid chars [8,

9]. Bio-oil, the major product from fast pyrolysis, is a potential liquid fuel that bio-oil derived from wood pyrolysis.

Flash pyrolysis is a pyrolysis process occurring at relatively high temperatures of above 700°C; at very high heating rates and similarly short residence times. It particularly maximizes gas yields with minimum liquid and char production.

2.4.5 BIOCHEMICAL PROCESSES

The process of bio-chemical conversion of biomass carried out by two main processes[8, 9].

They are,

1. Alcoholic fermentation
2. Anaerobic digestion or fermentation, for producing biogas.

2.4.5.1 ALCOHOLIC FERMENTATION:

The main products of this process are liquid fuel like ethanol that is produced by the process of fermentation from biomass materials which consist of sugars, starch or cellulose provides a high quality fuel for storage and transport [8, 9]. It should be noted that the biochemical conversion of woody wastes is more difficult for the fermentative degradation and need first to be broken down by acidic or enzymatic hydrolysis because of the presence of longer-chain polysaccharides. On the basis of energy utilization, product ethanol after distillation purification can be used as a supplement or substitute for petrol or gasoline in cars. Also, biomass materials for alcoholic fermentation are generally agricultural production/processing residues or energy crops. Molasses, a by-product of sugar-manufacturing process, has been industrially bio-converted for the production of ethanol.

2.4.5.2 ANAEROBIC DIGESTION:

Anaerobic digestion is the conversion or degradation of organic wastes through microbial actions in the absence of oxygen to reducing gases (biogas) that mainly consist of methane and carbon dioxide and contain various trace components such as hydrogen sulfide, acids and thiols. A typical example is the landfill gas (LFG) from the MSW buried in sanitary landfill sites. The collected LFG, which generally consists of up to 50% methane, can be purified and then burned in engines or turbines to produce heat and electricity [8, 9]. Practically, the biogas is commonly produced by using animal manure in an airtight container (digester). Due to the high heating value (5400–6000 kcal/Nm^3) of biogas, the biogas thus generated can be directly combusted in

burners for cooking, or used as gas fuel in internal combustion engines to generate electricity, or further upgraded to natural gas quality by the removal of carbon dioxide and hydrogen sulfide.

2.5 CONSTRAINTS ON USAGE OF BIO-MASS:

In nature, biomass is not concentrated, and so, the use of naturally occurring biomass requires transportation, which increases the cost and reduces the net energy production [11].

1. Biomass has a low bulk density, which makes transportation and handling difficult and costly.
2. The incomplete combustion of fuel wood produces organic particulate matter, carbon monoxide and other organic gases. If high temperature combustion is used, oxides of nitrogen will be produced.
3. The health impact of air pollution inside buildings is a significant problem in developing countries, where fuel wood is burnt inefficiently in open areas for domestic cooking and space heating.
4. There is the potential for widespread use of natural forests to cause deforestation and localized fuel wood scarcity with serious ecological and social ramifications.
5. The production and processing of biomass can involve significant energy input, such as fuel for agricultural vehicles and fertilizers, resulting in a poor energy balance for the biomass application.
6. Biomass processes need to minimize the use of energy intensive and fossil fuel based inputs and maximize waste and energy recovery.
7. There are often political and institutional constraints to biomass use, such as policies, taxes and subsidies that encourage the use of fossil fuels.
8. Energy prices often do not reflect the environ-mental benefits of biomass and other renewable energy resources.

2.6 BIO-MASS AND ITS FUTURE USES:

In the future, biomass has a great potential to provide a cost effective and sustainable supply of energy and helping reduce greenhouse emissions [11].

1. By the year 2050, it is estimated that 90% of the world population will live in developing countries and there is an urgent need that all the biomass processes used are sustainable and energy efficient.

2. Usage of advance technologies by which there is a increase in more efficiency of biomass production and conversion, might be one possible reason for the increased usage of biomass.
3. Biomass waste and residues are expected increase and can be substituted by energy crops in the longer term.
4. The success of the biomass derived chemicals industry will depend on the supply and demand for feedstock, primary chemicals and key intermediates the petrochemical industry cannot make, such as cellulose and lactic acid.
5. Electricity generation lies in biomass integrated by gasification/gas turbine technology, which offers high energy conversion efficiencies.
6. In future, Biomass may completely favour and act as a major feed stock chemical industry.
7. Biomass is a renewable, flexible and adaptable resource. Crops can be grown to satisfy changing end user needs.

2.7 Literature in de-oiled cakes:

De-oiled cake, which is one of the forms of agricultural residue, could be a potential source of raw material for extraction of bio fuels. The most effective way of extraction of bio fuels from these de-oiled cakes is pyrolysis and the literatures of the work carried out on these cakes, residues and engine performances of their transesterified bio-oils derived from seed are given below.

F. Karaosmanoglu et. al., [4] conducted slow pyrolysis experiments on straw and stalk of the rapeseed plant in a tubular reactor under the conditions of static atmosphere, varying temperatures of 350 ^{0}C, 450 ^{0}C, 550 ^{0}C and 650 ^{0}C and at heating rates of 10 ^{0}C min^{-1} and 30 ^{0}C min^{-1}. The maximum liquid yield was observed to be evolving at 650 ^{0}C pyrolysis temperature and at a heating rate of 30 ^{0}C min^{-1}.

S. Ucar et. al.,[12] investigated the composition of products from the pyrolysis of rapeseed oil cake in a fixed bed reactor at 400, 450, 500, 700 and 900 ^{0}C at a heating rate of 5 ^{0}C min^{-1} in nitrogen atmosphere. The maximum oil yield was obtained at a temperature of 550 ^{0}C.

K. Giannakopoulou et. al.,[13] studied on the method for the development of catalytic conversion of biomass into liquid products and their characterization in a batch and fixed bed

reactor. Rapeseed cake was used as raw material, while H-ZSM-5 and H-Beta zeolites were used as catalysts. They concluded that addition of catalysts in the conversion system reduced the liquid phase yield compared to the non-catalytic processes.

K. Giannakopoulou et. al.,[14] used H-ZSM-5, Fe-ZSM-5 and H-Beta, zeolite catalysts of three types to study the catalytic co-conversion of rapeseed cake and safflower oil under low pressure, at the temperatures of 350, 400 ^{0}C a heating rate of 6 ^{0}C/min. The liquid phase characteristics varied by the use of different catalysts.

N. Ozbay et. al.,[15] conducted fixed bed pyrolysis experiment is two kind of reactors namely tubular and a Heinze to study the effect of temperature on yields and chemical composition of products. The maximum oil yield of 29.68% was obtained in N_2 atmosphere at a pyrolysis temperature of 550°C with a heating rate of 7°C min^{-}1 in a tubular reactor.

E. Putun et. al.,[16] conducted catalyzed pyrolysis of cotton-seed cake for various contents (1, 5, 10, 20 wt.% of raw material) of zeolite at four different pyrolysis temperatures at sweeping gas flow rate isothermally. The maximum liquid yield obtained was 30.84% at a pyrolysis temperature of 550 ^{0}C with a sweeping gas in the presence of clinoptilolite as catalyst.

E. Putun et, al.,[17] conducted catalytic pyrolysis of cotton seed cake to evaluate the amounts of product yields in steam atmosphere and investigate the effects of both zeolite and steam on pyrolysis yields. Pyrolysis experiments were carried out upto a temperature range of 400 – 700 ^{0}C and the optimum temperature at which maximum yield of liquid product obtained was 500 ^{0}C. From the above experiments it was clear that pyrolysis experiments and characterization of products resulted in production of higher quality bio-oils by steam catalytic pyrolysis.

S.A.Raja et. al.,[18] conducted fluidized bed flash pyrolysis experiments by using jatropha oil cake to determine the effects of particle size, pyrolysis temperature and nitrogen gas flow rate on the pyrolysis yields. The maximum oil yield of 64.25 wt% was obtained at a nitrogen gas flow rate of 1.75m^3/h at a particle size of 0.7- 1.0 mm and pyrolysis temperature of 500 ^{0}C. Characterization of the liquid product showed that the bio-oil obtained may be used as a source of low-grade fuel directly or it may be upgraded to higher quality liquid fuel by thermocatalytic cracking or transesterification processes.

A.E. Putun et. al.,[19] have taken olive residues and pyrolysed it in a fixed bed reactor under different pyrolysis conditions to determine the effect of final temperature, sweeping gas flow rate

and steam velocity on the product yields and liquid product composition with a heating rate of 7 ^{0}C/min. The highest liquid product yield was obtained at 500 ^{0}C. Liquid product yield increased by using nitrogen and steam atmospheres. The results show that it is possible to obtain liquid products similar to petroleum from olive residue if the pyrolysis conditions are chosen accordingly.

S. Sensoz et. al.,[20] pyrolysed olive bagasse in a fixed-bed reactor to study the effects of temperature, heating rate, particle size and sweep gas flow rates on the yields of the products. Pyrolysis was done at temperatures between 350 and 550 ^{0}C with heating rates of 10 and 50 C min$^-$1. The particle size and sweep gas flow rate varied in the ranges 0.224–1.8 mm and 50–200 cm^3 min$^-$1, respectively. The bio-oil obtained at 500 ^{0}C was analyzed and at this temperature the liquid product yield was the maximum. The chemical characterization showed that the bio-oil obtained can be used chemical feedstock.

I. Demiral et. al.,[21] pyrolysed olive and hazelnut residues by using activated alumina and sodium feldspar as catalysts in a fixed-bed reactor. The maximum bio-oil yields for the bio-oils obtained from pyrolysis of olive bagasse were found as 37.07% and 36.67% on using activated alumina and sodium feldspar as catalysts, respectively, while these values were 27.64% and 31.68%, respectively, for the bio-oils from hazelnut bagasse.

B. B. Uzun et. al.,[22] carried out pyrolysis experiments using soya bean cake at temperatures ranging from 400 to 700 ^{0}C, for various nitrogen flow rates, heating rates and particle sizes. The maximum liquid yield was 42.83% at a pyrolysis temperature of 550 ^{0}C with a sweeping gas rate of 200 cm3 min$^-$1 and heating rate of 700 ^{0}C min$^-$1 for a soybean cake sample having 0.425 < Dp < 0.85 mm particle size.

2.8 ENGINE PERFORMANCE:

S. Godiganur et al.,[23] used blends of mahua oil methyl ester to study emission and performance characterstics in a cummins 6BTA 5.9 G2- 1, 158 HP rated power, turbocharged, DI, water cooled diesel engine. It was observed that by using mahua bio diesel, with the increase of biodiesel in the blends there was a significant reduction in CO, HC emissions and fuel consumption with slight increase in NOx emission. Brake specific energy consumption decreases and thermal efficiency of engine slightly increases when operating on 20% biodiesel.

S. Puhan et. al.,[24] transesterified mahua oil with methanol using sodium hydroxide as base catalyst and tested it in a single cylinder, four stroke, direct injection diesel engine to evaluate the performance and emissions. Engine performance results showed a slight power loss than diesel and increase in fuel consumption due to the lower heating value of the ester. Emissions of CO, HC are too low and oxides of nitrogen were slightly low for ester compared with diesel and proved that it could be used as alternative fuels in a diesel engine.

S. Puhan et al.[25] has done the transesterification of mahua oil with ethanol in presence of H_2SO_4 as an acid catalyst and tested it in a 4-stroke single cylinder natural aspirated direct injection diesel engine. Results showed that brake thermal efficiency of mahua oil ethyl ester is almost same. A reduction in emissions of carbon monoxide, hydrocarbons, oxides of nitrogen and bosch smoke number was observed.

B. Singh et. al.,[26] carried transesterification of spent oil using methanol and sulfuric acid (95%) as catalysts followed by bubble washing. Engine performance was conducted using a Prony brake internal combustion (IC) diesel engine using various blending ratios of biodiesel with commercial diesel to evaluate emission and performance characters tics. The results indicate that dual fuel with a blend of 8% biodiesel yielded good efficiency in the IC-diesel engines without the need for making any modifications in the engine.

N. Usta et. al.,[27] transesterified tobacco oil by using NaOH as catalyst and carried out engine tests in a turbocharged indirect injection diesel engine fuelled with diesel fuel No. 2 and tobacco seed oil methyl ester 10%, 17.5% and 25% blends. There was a decrease in CO, SO_2 emission as it contains about 11.4% oxygen by weight, and this oxygen helps to oxidize the combustion products in the cylinder. NOx emissions slightly increased due to higher combustion temperature.

A.N. Ozsezen et. al.,[28] used canola oil methyl ester (COME) and waste (frying) palm oil methyl ester (WPOME) to determine the performance and combustion characteristics in a constant engine speeds under the full load condition of the engine. It was found that, when the test engine was fueled with WPOME or COME instead of petroleum based diesel fuel (PBDF), the brake power reduced by 4–5%, while the brake specific fuel consumption increased by 9–10%. On the other hand, methyl esters caused reductions in carbon monoxide (CO) by 59–67%, in unburned hydrocarbon (HC) by 17–26%, in carbon dioxide (CO2) by 5–8%, and smoke

opacity by 56–63%. However, both methyl esters produced more nitrogen oxides (NOx) emissions by 11–22% compared with those of conventional diesel.

M. Pugazhvadivu et. al.,[29] used a non-edible waste frying vegetable oil, reducing its viscosity by preheating as an alternative fuel for diesel engine. It was observed that by using preheated WFO, the BSEC and brake thermal efficiency improved. The engine exhaust emissions such as CO and smoke were reduced considerably. Improvement in engine performance and maximum reduction in CO and smoke emissions was obtained using WFO (135 ^{0}C) to WFO (75 ^{0}C).

H. Hazar et. al.,[30] used raw rapeseed oil (RRO) and blended with diesel fuel (DF) by 50% and 20% and tested the fuel using in a single cylinder, four stroke, naturally aspirated, direct injection compression ignition engine. The results showed a highest value of decrease in BSFC by using of O50 blend. The exhaust gas temperature for O50 is fairly higher when compared with O20 and diesel fuel. The NOx emission lowers when RRO blends are used. The CO emission decreased for all test fuels with preheating due to the improvement in spray characteristics and better air–fuel mixing. Smoke density for all test fuels decreases with preheating. It was concluded that preheating test fuel slightly affects engine performance while it significantly reduces exhaust emissions when operating with vegetable oil.

M. Karabektas et al.,[31] studied performance parameters and exhaust emissions of a diesel engine fuelled with diesel fuel and cottonseed oil methyl ester(COME) in a one cylinder, four-stroke, direct injection diesel engine at full load conditions. The fuel was preheated before it is supplied to the engine. The results showed that brake power increased slightly with the preheating temperature up to 90 ^{0}C. When the COME is preheated to 120 ^{0}C, a considerable decrease in the brake power was observed. The results suggest that COME preheated up to 90 ^{0}C can be used as a substitute for diesel fuel.

M. Canakci et al.,[32] studied the combustion characteristics and emissions of two different petroleum diesel fuels (No. 1 and No. 2) and biodiesel from soybean oil in a four-cylinder turbocharged DI diesel engine at full load at 1400-rpm engine speed. The experimental results compared with No. 2 diesel fuel showed that biodiesel provided significant reductions in PM, CO, and unburned HC, the NOx increased by 11.2%. Biodiesel had a 13.8% increase in brake-specific fuel consumption due to its lower heating value. However, using No. 1 diesel fuel gave better emission results, NOx and brake-specific fuel consumption reduced by 16.1% and 1.2%,

respectively. The results indicated that biodiesel may be blended with No. 1 diesel fuel to be used without any modification on the engine.

M. Canakci et al,[33] studied the combustion and emission properties of preheated crude sunflower oil (PCSO) against diesel (PBDF) in a naturally aspirated, indirect injection (IDI) engine. Results showed that the cylinder gas pressure and heat release curves for PCSO at 75 ^{0}C were similar to those of PBDF. The brake specific fuel consumption increased by almost 5%. The emission test results showed that the decreases in CO_2 emissions and smoke opacity 2.05% and 4.66%, HC and CO emissions increased by 34% and 1.77%.

P.K. Sahoo et al,[34] tested jatropha, karanja and olanga oils and their blends (20 and 50 by v%) by varying loads (0, 50 and 100%) for combustion analysis. The results revealed that neat Polanga biodiesel that results in maximum peak cylinder pressure was the optimum fuel blend as far as the peak cylinder pressure was concerned. The ignition delays were consistently shorter for neat Jatropha biodiesel, varying between 5.9^0 and 4.2^0 crank angles lower than diesel with the difference increasing with the load. They suggested that furthe research and development on the additional fuel property measures, long-term run and wear analysis of biodiesel fueled engine is also necessary along with injection timing and duration for better combustion of biodiesel in diesel engines.

CHAPTER - 3
EXPERIMENTAL

EXPERIMENTAL:

3.1 MATERIAL

The raw materials neem cake, mustard cake and mahua cake have been collected in the form of solid from the nearest oil mills. The proximate, ultimate analysis and oil content of all the three cakes are shown in Table.6 and are compared with rapeseed and soya bean cakes. Soxhlet apparatus was used to find the oil content of the raw material. The solvent used for oil extraction was petroleum ether. The oil content of neem cake was 3.2%, mustard cake was 10.2%, and mahua cake is 5.7%.

3.2 PYROLYSIS PROCEDURE:

Pyrolysis experiment was carried out at a temperature of 350, 400, 450, 500, 550 and 600 ^{0}C for neem, sesame, mahua cake and 350, 400, 450, 500, 550, 600, 650, and 700 ^{0}C for mustard cake. Pyrolysis is done in a reactor which is made of SS (316) material with diameter 4.5 cm and height 18.5 cm is placed in electric furnace. The temperature of the furnace is maintained by a highly sensitive PID controller. Pyrolysis experiment was done by taking 30gms of the raw material of particle size of 3mm is taken in the reactor and the temperature is raised at a rate of 25 ^{0}C/min. The liquid products were condensed by cooling with ice bath. The temperature is measured by a Cr-Al: K type thermocouple fixed inside the reactor and in the furnace, one can attain a temperature of 1200 ^{0}C. Figure. 2 Shows the schematic diagram of the pyrolysis experimental set-up.

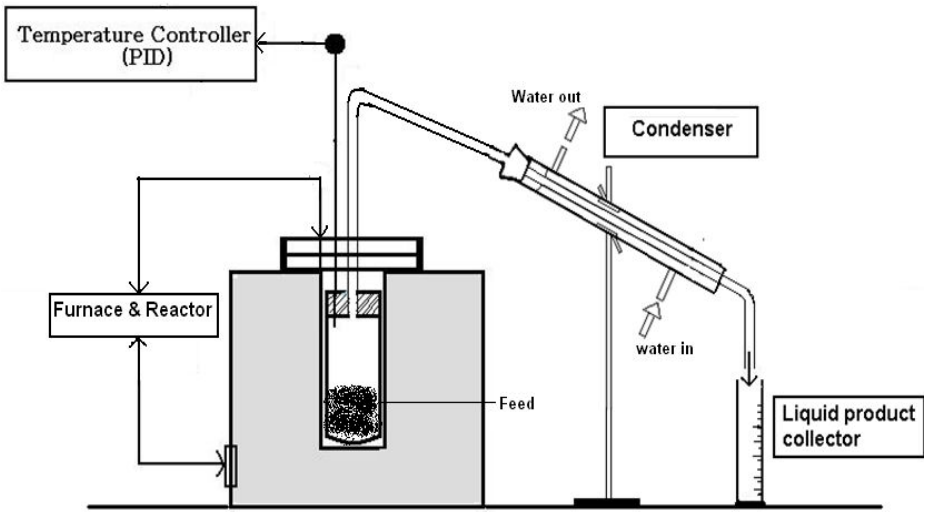

Figure. 2. Schematic diagram of the pyrolysis experimental setup

Table. 6 Proximate, ultimate analysis and oil content of all the neem, mustard, mahua de-oiled cakes raw materials.

Property	Neem cake	Mustard cake	Mahua cake	Rapeseed cake	Soya bean cake
	Present Work			S. Ucar et. al.,[12]	B.B. Uzun et al.[22]
PROXIMATE ANALYSIS					
Moisture content	6.13	6.02	4.18	10.59	8.38
Volatile matter	79.26	84.02	88.38	67.31	71.60
Ash content	10.00	7.70	4.36	15.80	5.63
Fixed carbon	4.61	2.26	3.07	6.30	14.39
ULTIMATE ANALYSIS					
C	42.52	47.47	49.65	45.92	55.89
H	4.52	5.73	5.71	6.21	6.57
N	1.87	6.16	3.34	6.90	9.27
S	1.30	1.74	0.61	0.88	--
O	49.79	38.91	40.69	40.09	28.25
H/C molar ratio	1.28	1.45	1.38	1.62	1.41
O/C molar ratio	0.88	0.61	0.61	0.65	0.38
Oil content %	3.2	10.2	5.7	7.12	--
Empherical formulae	$CH_{1.275}N_{0.0375}S_{0.011}O_{0.878}$	$CH_{1.447}N_{0.111}S_{0.0137}O_{0.614}$	$CH_{1.379}N_{0.0576}S_{0.004}O_{0.614}$	$CH_{1.62}O_{0.65}N_{0.128}S_{0.007}$	$CH_{1.4}N_{0.14}O_{0.38}$
GCV(MJ/Kg)	18.2	20.5	21	19.84	23.23

3.3 CHARACTERIZATION:

3.3.1 Proximate And Ultimate Analysis:

The proximate analysis was done by ASTM D3173-75. The ultimate analysis was done by using Elementor CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a.

3.3.2 TGA:

TGA analysis of the sesame/neem/mustard/mahua cake was done by using **SHIMADZU TGA-60H** with nitrogen as carrier gas at a constant flow rate of 45 ml/min.

3.3.3 FTIR:

The pyrolytic oil obtained was analyzed for its functional by using **PERKIN ELMER RX.** The FTIR spectra were collected in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution.

3.3.4 1H- NMR:

1H-NMR spectra were recorded by using a 400 MHz, **BRUKER** DPX-400, High performance digital FT–NMR spectrometer by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

3.3.5 GC-MS:

The pyrolytic oil obtained was characterized by using **GC/MS- QP 2010 SHIMADZU**, equipped with flame ionization and mass spectrometry detection (GC-FID-MS).

3.3.6 SEM-EDX:

Scanning electron microscopy images were taken by using **JEOL (JSM-6480 LV)** microscope with an acceleration voltage of 15 kV.

3.3.7 ENGINE PERFORMANCE:

KIRLOSKAR TAF 1 model engine, with break power 4.4 KW, 1500 rpm rated speed, and has a compression ratio 17.5:1 was used and specifications are given in Table.7

Table.7 Engine specifications

Make/Model	Kirloskar TAF 1
Brake power, kW	4.4
Rated speed, rpm	1500
Bore [mm]	80
Stroke [mm]	110
Compression Ratio	17.5:1
Nozzle Opening Pressure [bar]	200
Injection Timing [^{o}CA]	23

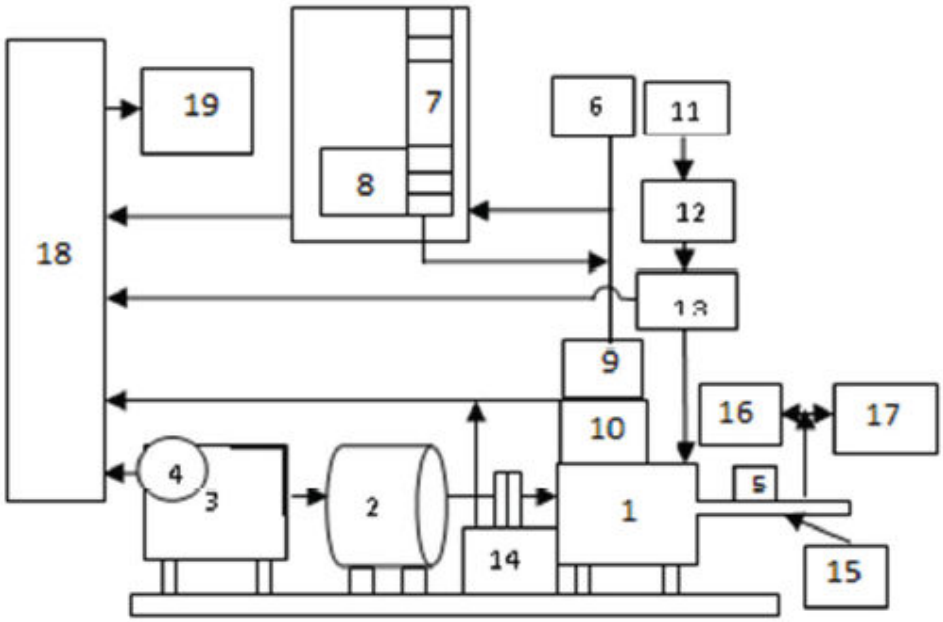

Figure.3 shows the schematic diagram of the experimental setup. The engine [1] was coupled to an alternator [2] to provide the loading and labeling is given in Table.8

Table.8 Label of engine parts

S.No	Name	S.No	Name
1	Engine	10	Fuel pump
2	Alternator	11	Air filter
3	Control panel	12	Air box
4	Load switch	13	Air flow sensor
5	Thermo couple	14	Speed sensor
6	Fuel tank	15	Exhaust pipe
7	Burette	16	Gas analyser
8	Fuel sensor	17	Smoke meter
9	Fuel filter	18	Computer with data acquisition system

CHAPTER - 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSIONS:

4.1 ANALYSIS OF SOLID PRODUCT BY TGA:

Thermogravimetric analysis (TGA) is used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. All experiments with TGA comprise three main different phases: drying, devolatilization in inert atmosphere and combustion in oxygen [35]. The measurement is normally carried out in air or in an inert atmosphere, such as helium or argon, and the weight is recorded as a function of increasing temperature. In nitrogen, moisture and volatiles are lost at temperatures up to 900 ^{0}C, and fixed carbon is burnt in oxygen leaving the ash as a residue. TGA analysis was done by using Shimadzu TGA 60H with nitrogen as carrier gas at a constant flow rate of 45 ml/min. The sample weighing 25 mg was heated from an initial temperature of 30 ^{0}C to 600 ^{0}C at a heating rate of 25 ^{0}C/min for residence time of 5 min.

DECOMPOSITION OF NEEM, MUSTARD ND MAHUA CAKE:

The comparative study of thermogravimetric analysis of neem, mustard and mahau cake is shown in Figure. 4. The thermal degradation of all the cake showed three weight loss regions. The first weight loss step for neem, mustard and mahua cake occurred at the temperature range of 70 – 120 ^{0}C, where moisture content in the cake was removed. The second weight loss step occurred at the temperature range between 120 – 230^{0}C where volatilization of hemicelluloses and residual oil occurs. Major weight loss occur from 230 to 600^{0}C with the inflection point at 320 ^{0}C, 350 ^{0}C, 380 ^{0}C where maximum rate of weight loss occurs which may be due to degradation of cellulose and lignin.

4.2 EFFECT OF PYROLYSIS TEMPERATURE ON PRODUCT YIELDS:

4.2.1 Effect of pyrolysis temperature on product yields of neem, mustard an mahua cake:

Figure. 5,6,7 shows the product yields for the pyrolysis of neem, mustard and mahua cake in relation to final temperature of pyrolysis at heating rate of 25^{0}C/min. Table. 9, 10, 11 shows the product distribution of pyrolysis of neem, mustard and mahua cake. The liquid product obtained was reddish-brown in color with an irritant odor and has a clear phase separation when stored in bottles.

1. The liquid product yield was 17.9% at the pyrolysis temperature of 350 ^{0}C and it increased to a maximum of 40.2% at a temperature of 400 ^{0}C. At the final pyrolysis temperature of 600 ^{0}C, the liquid yield decreased to 21.4%.
2. The yield of char decreased from 60.7% to 36.5% when the final pyrolysis temperature was increased from 350 to 600 ^{0}C.
3. The yield of volatiles or gaseous products decreased from 21.4 % to 8.5% when the final pyrolysis temperature was increased from 350 to 400 ^{0}C where maximum oil yield was obtained and then increased to 42 % at the final pyrolysis temperature of 600 ^{0}C.
4. As the temperature increased, reaction time decreased.

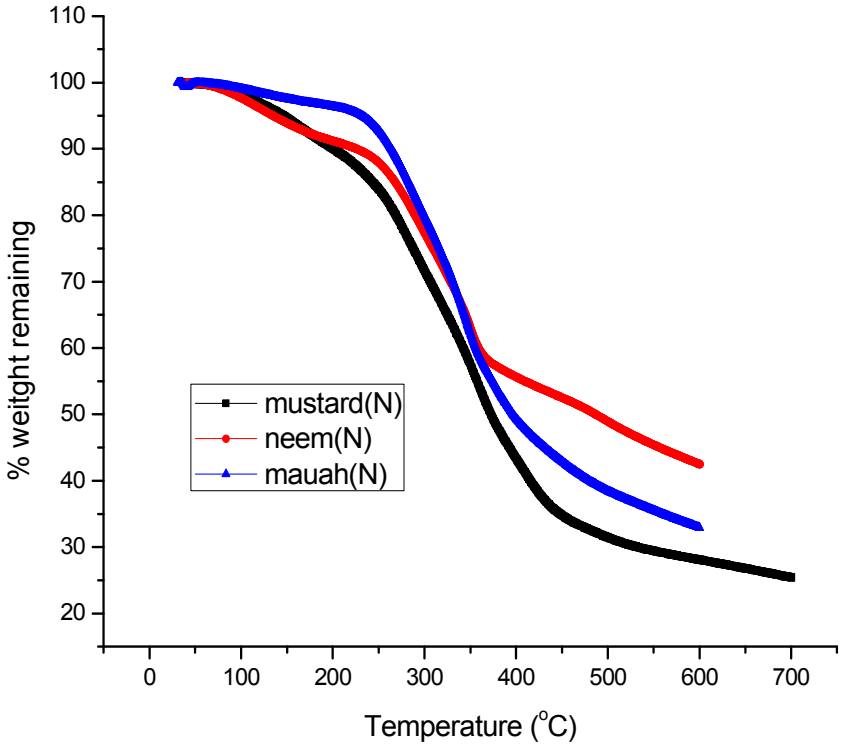

Figure. 4 The thermal degradation of neem, mustard and mahua cake

Table. 9 Product distribution of pyrolysis of neem cake:

Characteristic	Neem Cake					
Temperature (^{0}C)	350	400	450	500	550	600
Liquid product (%)	17.89	40.23	38.17	36.89	32.07	21.43
Char (%)	60.67	51.181	45.82	42.31	40.23	36.55
Volatiles (%)	21.42	8.58	15.99	20.79	27.68	42.00
Reaction time(min)	35	30	28	26	24	20

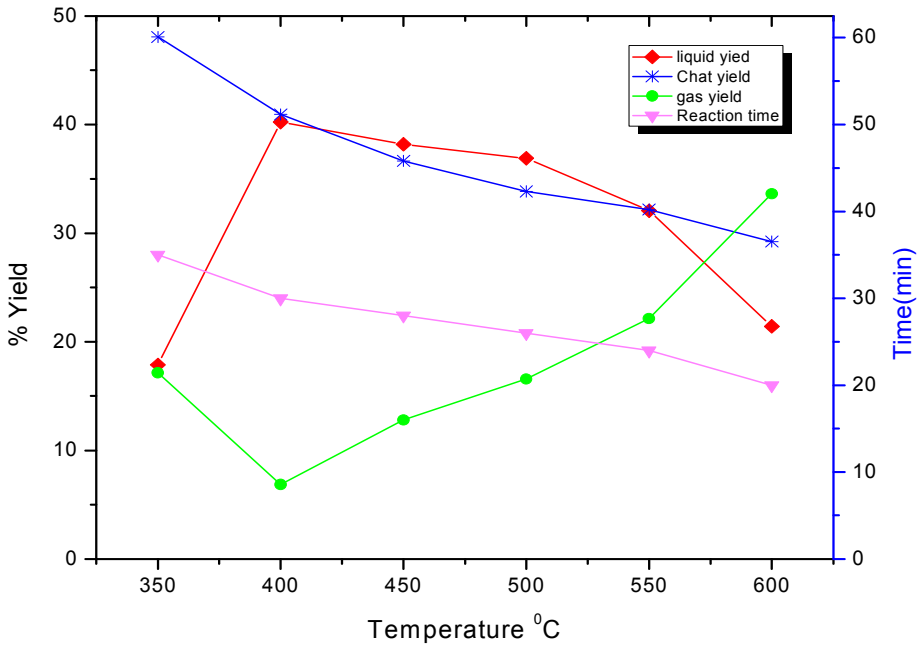

Figure. 5 Product yields for the pyrolysis of neem cake in relation to temperature

4.2.2 Mustard cake:

1. The liquid product yield was 23.4% at the pyrolysis temperature of 350 ^{0}C and it increased to a maximum of 53.2% at a temperature of 550 ^{0}C. At the final pyrolysis temperature of 700 ^{0}C, the oil yield decreased to 45.2%.
2. The yield of char decreased from 60.1% to 25% when the final pyrolysis temperature was increased from 350 to 700 ^{0}C.

3. The yield of volatiles or gaseous products decreased from 16.4 % to 12.5% when the pyrolysis temperature was increased from 350 to 400 ^{0}C and then increased to 29.7 % at the final pyrolysis temperature of 700 ^{0}C.
4. As the temperature increased, reaction time decreased.

Table. 10 Product distribution of pyrolysis of mustard cake:

Characteristic	Mustard cake							
Temperature (^{0}C)	350	400	450	500	550	600	650	700
Liquid product (%)	23.39	41.27	45.82	50.41	53.26	52.09	50.00	45.23
Char (%)	60.13	46.13	39.67	33.39	29.97	28.98	27.82	24.96
Volatiles (%)	16.47	12.59	14.49	16.18	16.76	18.92	22.17	29.79
Reaction time(min)	45	38	33	29	27	25	19	13

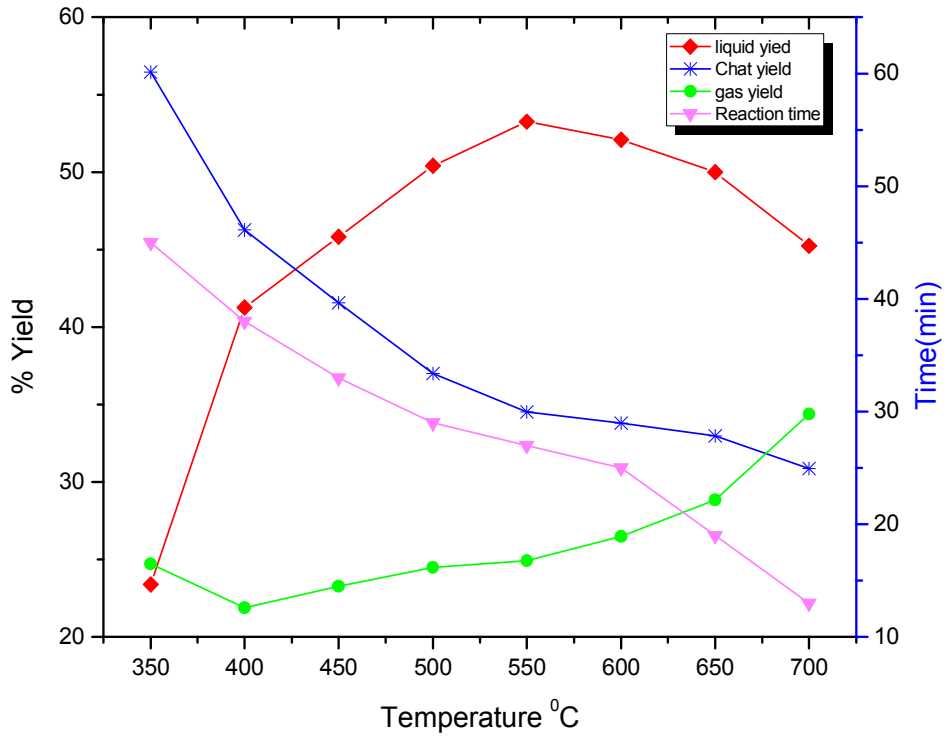

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Figure. 6 Product yields for the pyrolysis of mustard cake in relation to temperature

4.2.3 Mahua cake:

1. The liquid product yield was 21.6% at the pyrolysis temperature of 350 ^{0}C and it increased to a maximum of 41.3% at a temperature of 550 ^{0}C. At the final pyrolysis temperature of 600 ^{0}C, the oil yield decreased to 30.3%.
2. The yield of char decreased from 60.6% to 30.7% when the final pyrolysis temperature was increased from 350 to 600 ^{0}C.
3. The yield of volatiles or gaseous products decreased from 17.6 % to 16.5% when the pyrolysis temperature was increased from 350 to 400 ^{0}C and then increased to 39.2 % at the final pyrolysis temperature of 600 ^{0}C.
4. As the temperature increased, reaction time decreased.

Table.11 Product distribution of pyrolysis of mahua cake:

Characteristic	Mahua cake					
Temperature (^{0}C)	350	400	450	500	550	600
Liquid product (%)	21.68	27.10	33.28	41.27	41.36	30.03
Char (%)	60.67	56.30	49.42	36.28	33.00	30.76
Volatiles (%)	17.65	16.59	17.30	22.45	25.64	39.21
Reaction time(min)	28	24	21	20	19	17

From the above, it is clear that with increase in temperature, yield of liquid product increased upto a maximum temperature of 400 ^{0}C ,550 ^{0}C for neem and mustard and mahua cake respectively, and then decreased and this is due to rapid devolatilization of cellulose and hemicelluloses. The gaseous yield decreased initially then increased with increase in temperature. This is may be due to secondary cracking of the pyrolysis vapors at higher temperatures. The yield of char decreased with increase in temperature. The decrease in the char yield with increasing temperature could be either due to greater primary decomposition or depolymerization of mustard cake to primary volatiles at higher temperatures and may be due to secondary decomposition of the char residue. Due to all the above reasons reaction time also decreased.

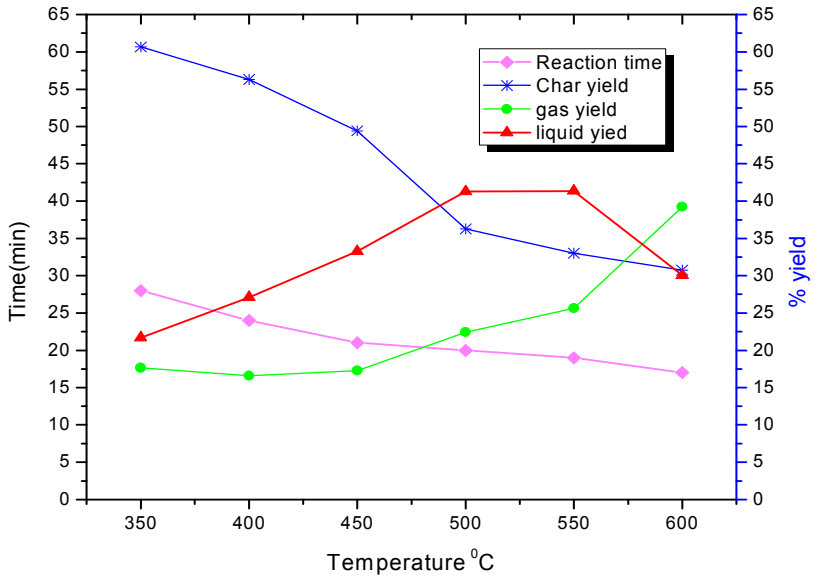


Figure.7 Product yields for the pyrolysis of mustard cake in relation to temperature

4.3 CHARACTERIZATION:

4.3.1 CHNS analysis of neem, mustard and mahua cake pyrolytic oil:

Elemental analysis of neem cake pyrolytic oil was done to find the elemental composition of bio-oil and to determine its empherical formula and are compared with diesel in Table.12.

Table.12 Ultimate analysis of neem, mustard and mahua cake pyrolytic oil

Element	Neem cake pyrolytic oil	Mustard cake pyrolytic oil	Mahua cake pyrolytic oil	Diesel
C	73.81	58.46	63.20	85.72
H	8.79	8.52	8.74	13.2
N	1.88	5.86	4.04	0.18
S	0.83	1.42	0.38	0.3
O	15.00	25.74	23.64	0.6
H/C molar ratio	1.43	1.75	1.66	1.85
Empherical formula	$CH_{1.4345}N_{0.021}$ $S_{0.0042}O_{0.153}$	$CH_{1.748}N_{0.0859}$ $S_{0.009}O_{0.330}$	$CH_{1.659}N_{0.054}$ $S_{0.0022}O_{0.280}$	$CH_{1.847}N_{0.0017}$ $S_{0.0013}O_{0.0052}4$
Calorific value MJ/ Kg	30	25.1	26.3	43.8

4.3.2 NMR Analysis:

1H- NMR spectra were recorded by using a 400 MHz, **BRUKER DPX-400**, High performance digital FT–NMR spectrometer was done by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

1H-NMR band assignments corresponding to structural features of neem, mustard and mahua cake pyrolytic oil is given in Table 13. β- CH_3, CH_2 hydrogens attached to an aromatic ring were present in higher proportion in bio-oil and that accounts to 28.8 % for neem bio-oil, 23.6% for mustard bio-oil, 28.4 for mahua bio-oil. About 11.6% of hydrogen was attached to hydroxyl groups or ring-join methylene in neem bio-oil, 15.8% in mustard bio-oil, 17% in mahua bio-oil. CH_2 and CH_β to an aromatic ring (naphthenic) and CH_3 γ or further from an aromatic ring were also present. Hydrogens attached to phenolic (OH) or olefinic were also present upto 5.3% in neem bio-oil, 2% in mustard and 1% in mahua bio-oil. But hydrogen attached to aromatics or conjugated olefins were not present and the spectrum are given in Figure. 8, 9, 10.

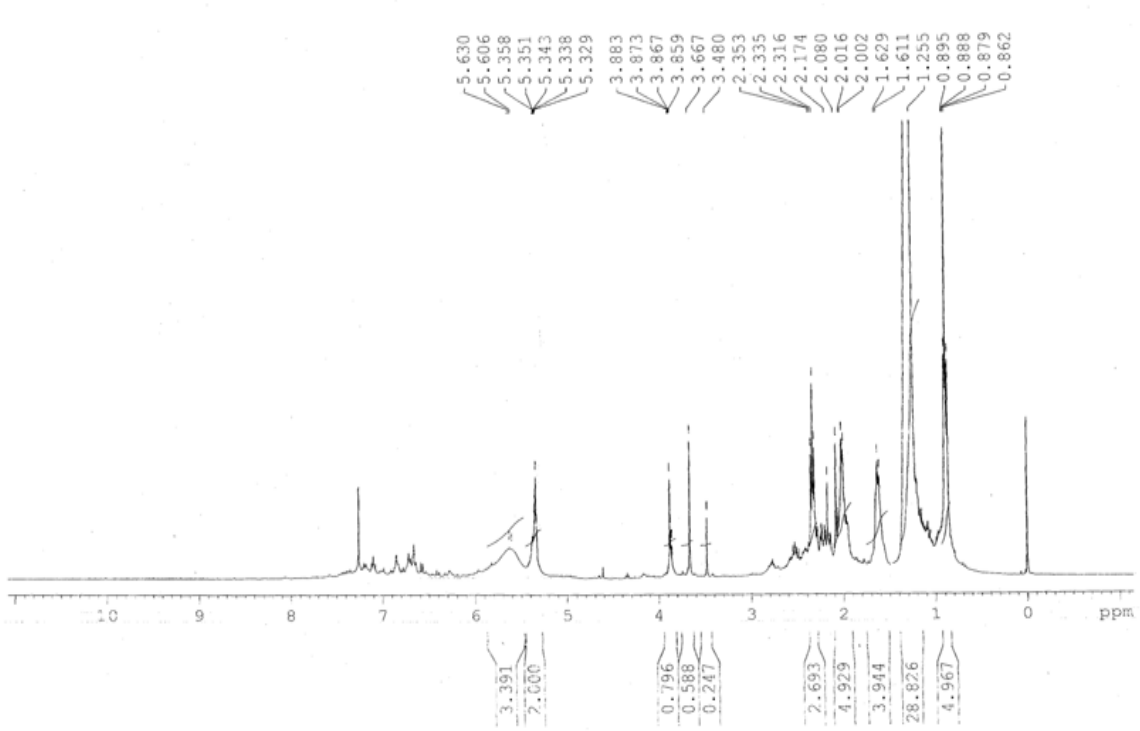


Figure.9 1H-NMR spectrum of neem cake pyrolytic oil.

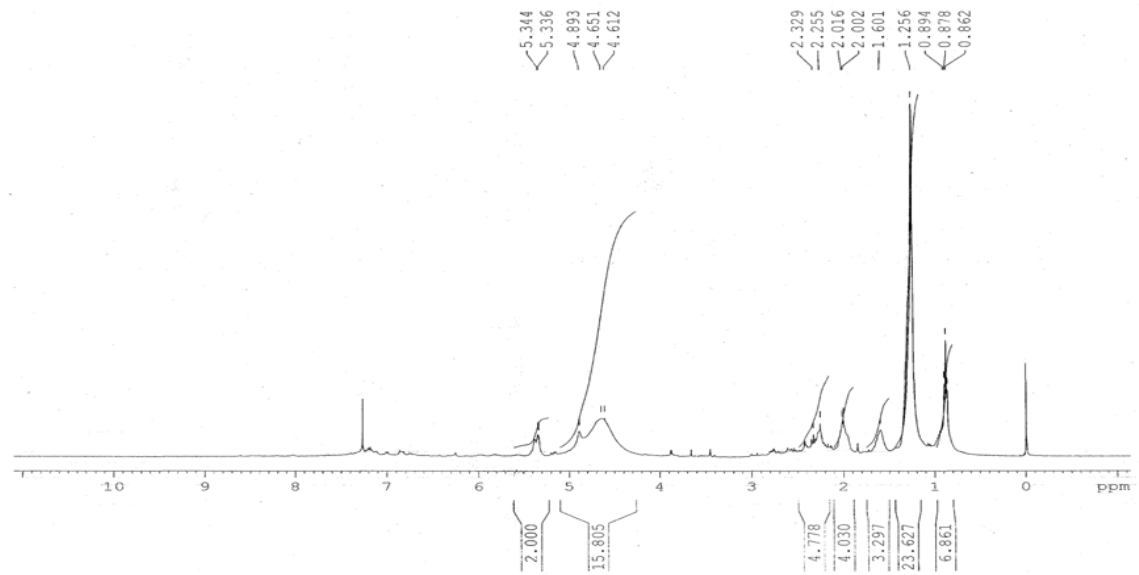


Figure.9 1H-NMR spectrum of mustard cake pyrolytic oil.

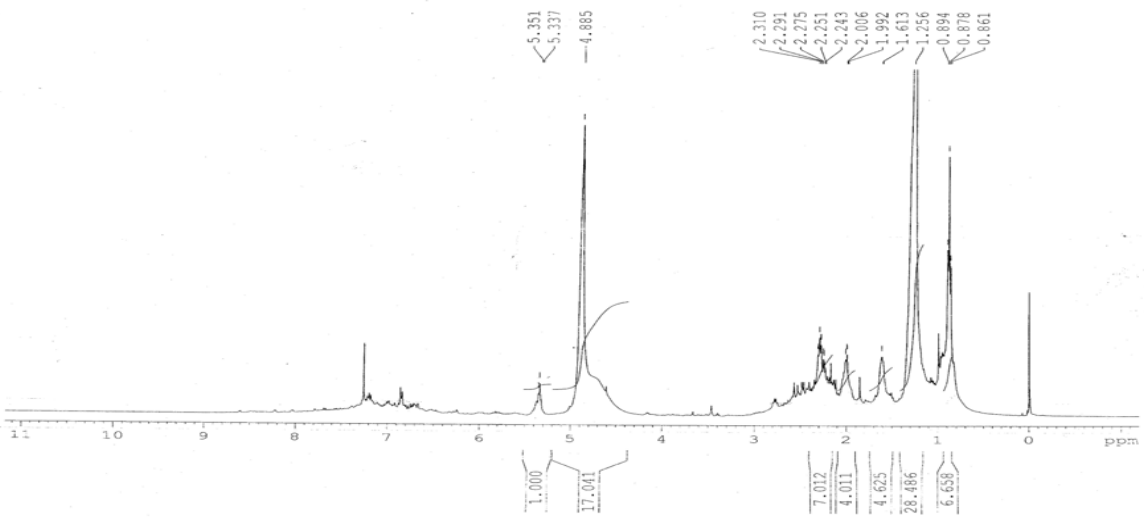


Figure.10 1H-NMR spectrum of mahua cake pyrolytic oil.

Table. 13 1H -NMR results of neem, mahua, mustard cake pyrolytic oil

Type of hydrogen	Chemical shift (ppm)	Percentage of Total Hydrogen (%)			
		Mustard	Neem	Mahua	Soybean
Phenolic (OH) or olefinic proton	6.5– 5.0	2	5.3	1	1.05
Hydroxyl groups or ring-join methylene (Ar–CH2– Ar)	4.5– 3.3	15.8	11.6	17.0	6.61
CH3 CH2 and CH to an aromatic ring	3.3– 2.0	4.7	2.6	7.0	29.32
CH2 and CH β to an aromatic ring (naphthenic)	2.0– 1.6	7.3	8.8	8.6	6.23
β-CH3, CH2 and CH γ to an aromatic ring	1.6– 1.0	23.6	28.8	28.4	24.36
CH3 γ or further from an aromatic ring	1.0– 0.5	6.8	4.9	6.6	19.89

4.3.3 FTIR Analysis

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in oil. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. Based on this principle functional group present in the pyrolytic oil were identified. The FTIR spectra were collected in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution. The FTIR imaging is carried out using Perkin Elmer RX.

4.3.3.1 Neem cake pyrolytic oil:

The presences of alkanes are detected at 2922.46, 2852.2 cm^{-1} with C-H stretching. C=O stretching vibrations at 1708.2 cm^{-1} shows the presence of aldehydes and ketones. C-H deformation vibrations at 1459.8 cm^{-1} detect the presence of alkanes. O-H bending vibrations at 1376.4 cm^{-1} show the presence of alcohols and phenols. The presence of amines is detected by C-N stretching vibrations and the presence of acids, esters, ether and alcohols by C-O stretching vibrations at 1212.39, 1110.4 cm^{-1}. Presence of alkenes was detected by C-H bending vibrations at 721.4 cm^{-1}. The functional groups present in the bio oil were identified and are tabulated in Table.14 and the comparison plots is given in Figure.11

Table. 14 Functional groups present in neem cake pyrolytic oil

Wave number(cm^{-1})	Type of vibration		Nature of functional group
721.43	C-H	Bending	Alkenes
1110.74	C-O	Stretching	Acid, Ester, Ether, Alcohol
1212.39	C-O	Stretching	Acid, Ester, Ether, Alcohol
	C-N	Stretching	Amines
1376.4	O-H	Bending	Alcohols and phenols
1459.84	C-H	Deformation	Alkanes
1708.25	C=O	Stretching	Aldehydes/Ketones
2852.26	C-H	Stretching	Alkanes
2922.56	C-H	Stretching	Alkanes

4.3.3.2 Mustard cake pyrolytic oil:

The N-H weak vibrations at 3392.3 cm^{-1} indicates the presence of amines. The presences of alkanes are detected at 2922.46 and 2851.2 cm^{-1} with C-H stretching. O-H stretching at 2558.8 cm^{-1} shows the presence of carboxylic acids and derivatives. C=C stretching vibrations at 1649.6 cm^{-1} shows the presence of alkanes. The presence of nitro group was detected by N=O asymmetric stretch vibrations at 1539.9 cm^{-1}. C-H bending or scissoring vibrations at 1455.4 cm^{-1} detect the presence of alkanes. The functional groups present in the bio oil were identified and are tabulated in Table.15.

Table.15 Functional groups present in mustard cake pyrolytic oil

Wave number (cm^{-1})	Type of vibration		Nature of functional group
1455.45	C-H	Bending/ scissoring	Alkanes
1539.94	N=O	Asymmetrical stretch	Nitro Compounds
1649.63	C= C	Stretching	Alkenes
2558.88	O-H	Stretching	Carboxylic acids and derivatives
2851.27	C-H	Stretching	Alkanes
2921.83	C-H	stretching	Alkanes
3392.34	N-H	Weak	Amines

4.3.3.3 Mahua cake pyrolytic oil:

The N-H weak vibrations at 3413.44 cm^{-1} indicates the presence of amines. O-H stretching at 2336.08 and 2558.8 cm^{-1} shows the presence of carboxylic acids and derivatives. C=C stretching vibrations at 1632.47 cm^{-1} shows the presence of alkenes. C-H bending/stretching vibrations at 667.7 cm^{-1} detect the presence of alkanes. The results were found consistent with the literature and when compared with GC-MS.

Table.16 Functional groups present in mahua cake pyrolytic oil

Wave number (cm^{-1})	Type of vibration		Nature of functional group
667.71	C - H	Bending/Stretching	Alkanes
1632.47	C= C	Stretching	Alkenes
2336.08	O-H	Stretching	Carboxylic acids and derivatives
2356.93	O-H	Stretching	Carboxylic acids and derivatives
3413.44	N-H	Weak	Amines

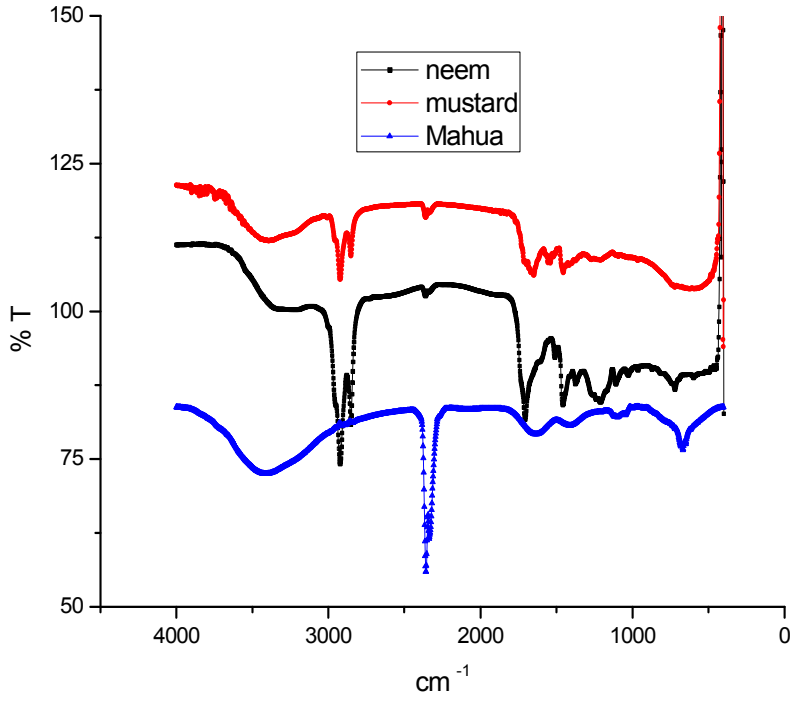


Figure.11 FTIR spectrum of neem, mustard and mahua bio-oil.

4.3.4 GC-MS

GC-MS is used both for the qualitative identification and for the quantitative measurement of volatile and semi volatile organic compounds in complex mixtures. The pyrolytic oil obtained was characterized by using GC/MS- QP 2010 SHIMADZU, equipped with flame ionization and mass spectrometry detection (GC-FID-MS). A capillary column coated with a 0.25 um film of DB-5 with length of 30 m and diameter 0.25 mm was used. The GS was equipped with a split injector at 200 ^{0}C with a split ratio of 1:10. Helium gas of 99.995% purity was used as carrier gas at flow rate of 1.51 ml/min. The oven initial temperature was set to 70 ^{0}C for 2 min and then increased to 300 ^{0}C at a rate of 10^{0}C/min and maintained for 7 min. All the compounds were identified by means of the NIST library. Mass spectrometer was operated at an interface temperature of 240 ^{0}C with ion source temperature of 200 ^{0}C of range 40-1000 *m/z*.

The major compound of neem cake and mustard cake pyrolytic oil, characterized by GC-MS at a pyrolytic temperature of 400^{0}C and 550 ^{0}C is given in Table.17,18. Different types of compounds such as normal alkanes, alkenes, saturated fatty acids and their derivatives: esters, amides and nitriles were identified. All the compounds were classified with increase in retention time. Figure 12,13 shows the GC-MS images of neem and mustard cake pyrolytic oil.

4.3.4.1 Neem cake pyrolytic oil:

Three major peaks was obtained at an area% of 49.60, 14.08, 10.24 and the compounds were identified as Phenol, m-pentadecyl ($C_{21}H_{36}O$), n-hexadecanoic acid ($C_{16}H_{32}O_2$), Octadec-9-enoic acid ($C_{18}H_{36}O_2$) resp. Phenol m-pentadecyl is used as a raw material for surfactants, antioxidants, anticorrosive: lubricant additives, cosolvent for insecticides, germicides; coupling agent. n-hexadecanoic acid (palmitic acid) is one of the most common saturated fatty acid used as enzyme inhibitor. Enzyme inhibitors are agents that combine with an enzyme in such a manner as to prevent the normal substrate-enzyme combination and the catalytic reaction. Octadec-9-enoic acid (Oleic acid) is a monounsaturated omega-9 fatty acid, used as an emulsifying or solubilizing agent in aerosol products.

4.3.4.2 Mustard cake pyrolytic oil:

The major compound of bio-oil, characterized by GC/MS at a pyrolytic temperature of 550 ^{0}C. Different types of compounds such as normal alkanes, alkenes, phenols, saturated fatty acids and their derivatives: esters, amides and nitriles were identified. All the

compounds were classified with increase in retention time. Four major peaks was obtained at an area% of 24.55, 11.36, 10.06, 9.4 and the compounds were identified as 9-octadecenoic acid($C_{18}H_{34}O_2$), Octadecanoic acid ($C_{18}H_{36}O_2$), 1-nonadecene($C_{19}H_{38}$) and hexadecanamide($C_{16}H_{33}NO$) resp. 9-octadecenoic acid (Oleic acid) is a monounsaturated omega-9 fatty acid, used as an emulsifying or solubilizing agent in aerosol products.

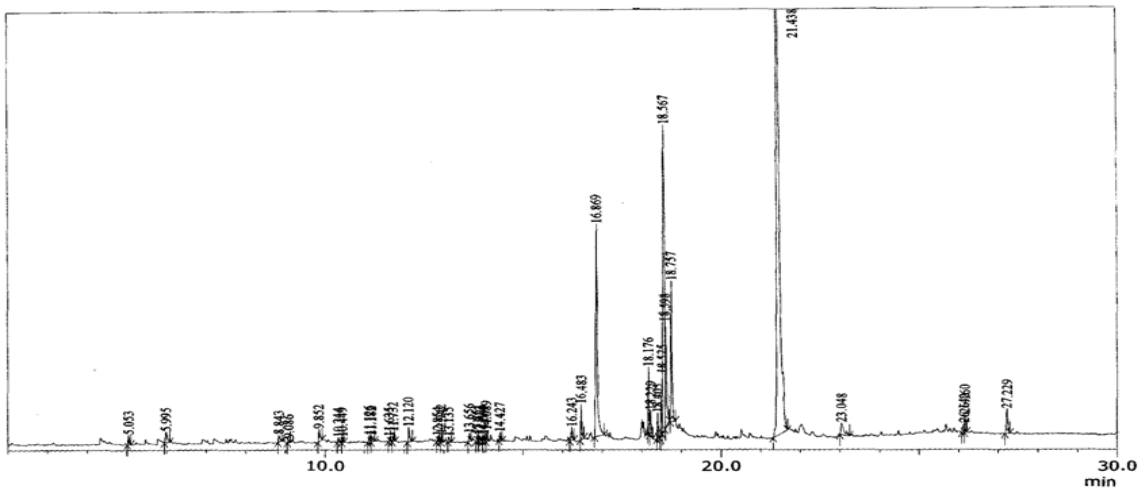


Figure.12 Spectrum of GC of neem cake pyrolytic oil

Octadecanoic acid (Stearic acid) is the saturated fatty acid with an 18 carbon chain used as an ingredient in making candles, plastics, dietary supplements, oil pastels and cosmetics, and for softening rubber. Nonadecene is one of the major component containing (15.06%) in the production of rose oil in perfume industry. Hexadecanamide is used in production of N-(2-hydroxyethyl)hexadecanamide which reduces edema formation and inflammatory hyperalgesia.

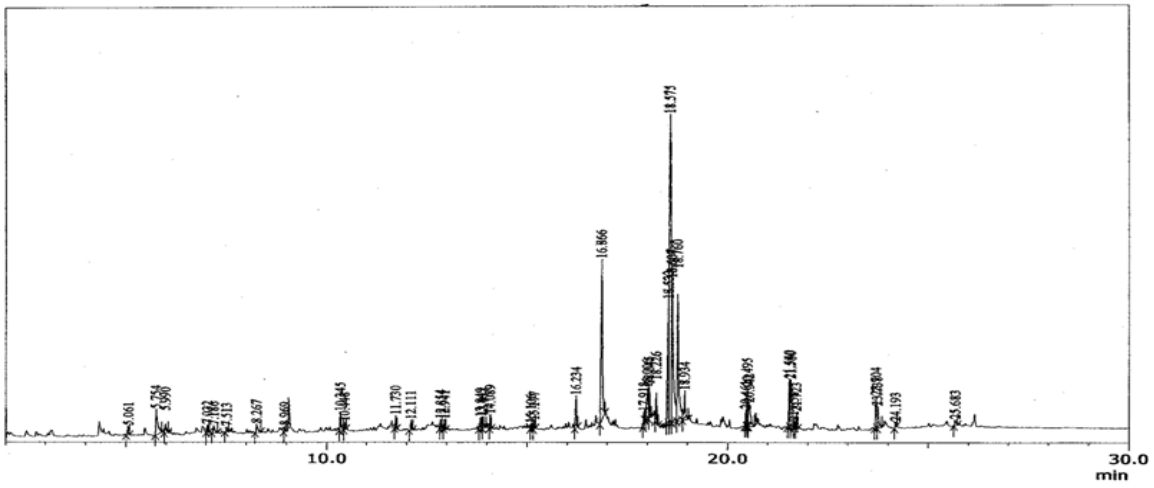


Figure.13 Spectrum of GC of mustard cake pyrolytic oil

Table.17 GC-Mass composition of the major compounds in bio-oils from pyrolysis of neem de-oiled cake.

R.Time	Area %	Name of compound	M.Formula
5.053	0.36	Cyclohexene, 1-methyl-4-(1-methylenenyl)-,(s)	$C_{10}H_{16}$
5.995	0.56	Phenol, 2-methoxy	$C_7H_8O_2$
8.843	0.28	Guaiacol, 4 ethyl	$C_9H_{12}O_2$
9.086	0.11	Tridecane	$C_{13}H_{28}$
9.852	0.59	Pyrogallol 1,3-dimethyl ether	$C_8H_{10}O_3$
10.344	0.19	1-Tetradecene	$C_{14}H_{28}$
10.449	0.14	Tetradecane	$C_{14}H_{28}$
11.126	0.28	1,2,4- Trimethoxybenzene	$C_9H_{12}O_3$
11.182	0.29	Phenol,2-methoxy-4-propenyl-,(E)	$C_{10}H_{14}O_2$
11.625	0.14	1-Pentadecene	$C_{15}H_{30}$
11.732	0.27	Pentadecane	$C_{15}H_{32}$
12.12	0.61	1,2,3-Trimethoxy-5-methylbenzene	$C_{10}H_{14}O_3$
12.854	0.16	1-Heptadecene	$C_{17}H_{34}$
12.942	0.21	Hexadecane	$C_{16}H_{34}$
13.135	0.18	2,4-Hexadienedioic acid, 3-methyl-4-propyl-,dimethyl ester	$C_{12}H_{18}O_4$
13.656	0.3	3-Phenyl propylbenzene	$C_{15}H_{16}$
13.851	0.22	3-Heptadecene,(z)	$C_{17}H_{34}$
13.912	0.21	3-Heptadecene,(z)	$C_{17}H_{34}$
14.009	0.17	1-Nonadecene	$C_{19}H_{38}$
14.089	0.3	Heptadecane	$C_{17}H_{36}$
14.427	0.29	[3,2-dimethyl-1-(2-phenylethyl)-4-pentyl]benzene	$C_{16}H_{18}$
16.243	0.59	Hexadecanenitrile	$C_{16}H_{31}N$
16.483	1.21	Hexadecanoic acid, methyl ester	$C_{17}H_{32}O_2$
16.869	10.24	n-Hexadecanoic acid	$C_{16}H_{32}O_2$
18.176	1.82	9-Octadecenoic acid, methyl ester,(E)	$C_{19}H_{36}O_2$
18.226	0.96	Heptadecanenitrile	$C_{17}H_{33}N$
18.405	0.75	Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$
18.567	14.08	Octadec-9-enoic acid	$C_{18}H_{34}O_2$
18.598	4.39	9-Octadecenoic acid	$C_{18}H_{34}O_2$
18.757	5.05	Octadecanoic acid	$C_{18}H_{36}O_2$
21.438	49.6	Phenol,m-pentadecyl	$C_{21}H_{36}O$
23.048	1.07	Phenol,3-pentadecyl	$C_{21}H_{36}O$
26.142	0.4	Quintozene	$C_6Cl_5NO_2$
26.16	0.61	Stigmast-5-en-3-yl 9-octadecenoate	$C_{35}H_{92}O_7$

Table.18 GC-Mass composition of the major compounds in bio-oils from pyrolysis of mustard de-oiled cake.

R.Time	Area %	Name of compound	Molecular formula
5.061	0.49	4 Methoxy phenol	C_7H_8O
5.754	2.53	Cyclohexanol,3,3,5-trimethyl	$C_9H_{18}O$
5.99	0.54	Pentylbenzene	$C_{11}H_{16}$
7.032	0.44	p-Ethylphenol	$C_8H_{10}O$
7.186	0.51	1-Undecanol	$C_{11}H_{24}O$
7.513	0.29	Benzenepropanenitrile	$C_{12}H_{11}ClN_2O$
8.267	0.68	1-Tridecene	$C_{13}H_{26}$
8.969	0.21	Indole	C_8H_7N
10.345	1.16	Teteadecane	$C_{14}H_{30}$
10.448	0.39	Pentadecane	$C_{15}H_{32}$
11.73	0.57	5-Tert-butylpyrogallol	$C_{10}H_{14}O_3$
12.111	0.51	1-Hexadecene	$C_{16}H_{32}$
12.854	0.4	Hexadecane	$C_{16}H_{34}$
12.941	0.42	1-Heptadecene	$C_{17}H_{34}$
13.849	0.63	3-Heptadecene,(z)	$C_{17}H_{34}$
13.911	0.67	Heptadecane	$C_{17}H_{36}$
14.089	0.57	1-Nonadecene	$C_{19}H_{38}$
15.106	0.23	Heneicosane	$C_{21}H_{44}$
15.177	0.33	Heptadecanenitrile	$C_{17}H_{33}N$
16.234	1.72	n-Hexadecanoic acid	$C_{16}H_{32}O_2$
16.866	10.06	1-Nonadecene	$C_{19}H_{38}$
17.918	0.55	Oleanitrile	$C_{18}H_{33}N$
18.006	2.16	Oleanitrile	$C_{18}H_{33}N$
18.045	1.69	Heptadecanenitrile	$C_{17}H_{33}N$
18.533	7.13	9-Octadecenoic acid	$C_{18}H_{34}O_2$
18.575	24.55	9-Octadecenoic acid	$C_{18}H_{34}O_2$
18.607	11.36	Octadecanoic acid	$C_{18}H_{36}O_2$
18.76	9.4	Hexadecanamide	$C_{16}H_{33}NO$
18.934	2.27	Methyl linoleate)	$C_{19}H_{34}O_2$
20.461	0.83	9-Octadecenamide	$C_{18}H_{35}NO$
20.495	2.04	9-Octadecenamide	$C_{18}H_{35}NO$
20.542	2.17	Oleanitrile	$C_{18}H_{33}N$
21.54	2.62	Oleanitrile	$C_{18}H_{33}N$
21.58	3.16	Methyl erucate	$C_{23}H_{44}O_2$
21.658	0.24	Nonadecanenitrile	$C_{19}H_{37}N$
21.723	0.69	9-Octadecenamide	$C_{18}H_{35}NO$
23.704	1.86	13-Docosenamide	$C_{22}H_{43}NO$
23.738	1.56	N,N- dimethyloctadecanamide	$C_{23}H_{48}N_2O$
25.683	0.38	Stigmast-5-en-ol, oleate	$C_{47}H_{82}O_2$

4.3.5 PHYSICAL PROPERTIES:

4.3.5.1 NEEM CAKE PYROLYTIC OIL:

Physical properties of neem cake pyrolytic oil (NCPO) were found out by standard test methods and are compared with crude neem oil (CNO), neem bio-diesel (NBD) and commercial diesel (CD) is given in Table.19. Distillation was also done to NCPO to find out its initial and final boiling point and was found to be 96 ^{0}C and 374 ^{0}C resp. Kinematic viscosity of NCPO is much greater than CD and this is due to the presence of glycerides or polymers that are found in cooking oil.

Table.19 Comparison of physical properties of crude neem oil, neem bio-diesel, neem cake pyrolytic oil and commercial diesel.

Characteristic	Neem Oil (CNO)	Neem bio-diesel (NBD)	Present work (NCPO)	Diesel (CD)
Appearance	Dark brown oil	Light to dark brown	Dark brown	Yellowish
Specific gravity(15C/15 C)	0.92	0.868	1.002	0.84
Kinematic viscosity@ 40 ^{0}C in cst	35.83	2.7	30	2.7
Conradson carbon residue	--	--	0.98	<0.15
Flash point (^{0}C)	100	76	48	60
Fire point (^{0}C)	109	81	56	65
Cloud point (^{0}C)	19	9	10	-40
Pour point (^{0}C)	10	2	2	-16
Gross calorific value(MJ/Kg)	44.65	35.2	30	42.5
Sulfur content	--	--	0.24	1.2
Distillation				
Initial boiling point			96	172
10 % recovery			176	194
20 % recovery			248	209
30 % recovery			292	226
40 % recovery			318	243
50 % recovery			332	260
60 % recovery			342	277
70 % recovery			352	296
80 % recovery			368	316
90 % recovery			372	341
Final boiling point			374	---
Residue			7.5	---
Loss%			0.5	---

4.3.5.2 MUSTARD CAKE PYROLYTIC OIL:

Physical properties of mustard cake pyrolytic oil (MCPO) were found out by standard test methods and are compared with crude mustard oil (CMO), mustard bio-diesel (MBD) and commercial diesel (CD) is given in Table.20. Distillation was also done to MCPO to find out its initial and final boiling point and was found to be 90 ^{0}C and 350 ^{0}C resp.

Table.20 Comparison of physical properties of crude mustard oil, mustard bio-diesel, mustard cake pyrolytic oil and commercial diesel.

Characteristic	Mustard oil (CMO)	Mustard Biodiesel(MBD)	Present work (MCPO)	Diesel (CD)
Appearance	Dark brown oil	--	Dark brown oil	Yellowish
Specific gravity(15C/15 C)	0.98	0.874	1.022	0.84
Kinematic viscosity@ 40 C in cst	41.23	5.33	49.3	2.7
Conradson carbon residue	--	--	2.49	<0.15
Flash point (^{0}C)	215	170	44	60
Fire point (^{0}C)	--	--	52	65
Cloud point (^{0}C)	--	-2	1	-40
Pour point (^{0}C)	-16	-9	-2	-16
Gross calorific value(MJ/Kg)	36.9	39.62	25.1	42.5
Sulfur content %	18(ppm)	11 (ppm)	0.49	1.2
Distillation				
Initial boiling point			90	172
10 % recovery			96	194
20 % recovery			98	209
30 % recovery			110	226
40 % recovery			244	243
50 % recovery			288	260
60 % recovery			322	277
70 % recovery			330	296
80 % recovery			342	316
90 % recovery			-	341
Final boiling point			350	---
Residue			11	---
Loss%			1	---

4.3.6 PROXIMATE AND ULTIMATE ANALYSIS OF CHAR

Proximate and ultimate analysis of mustard, neem and mahua cake char was done to determine the presence of volatile matter and characterized for its elemental composition by CHNS analysis and are tabulated in Table.21. Its Empherical formula, calorific value was also determined. It was found that even after pyrolysis still some volatile matter was present in the char and it was found to be maximum in mahua and neem char. This shows that pyrolysis is not done completely. Carbon content was found to be almost same in all the char.

Table.21 Proximate and ultimate analysis of mustard, neem and mahua cake char

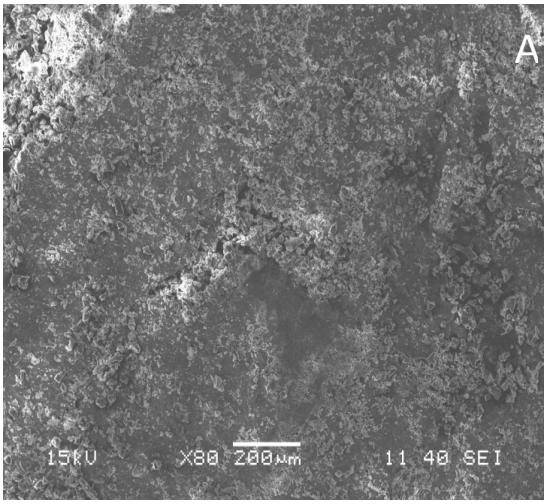
Property	Neem char	Mustard char	Mahua char
Proximate Analysis			
Moisture content	3.70	4.80	4.25
Volatile content	32.00	21.00	39.30
Ash content	24.50	28.10	22.29
Fixed carbon	39.80	46.10	34.17
Ultimate analysis			
C	82.34	85.43	70.14
H	7.89	4.79	2.98
N	5.76	6.17	4.43
S	0.44	0.20	0.59
O	3.57	3.41	21.85
H/C molar ratio	1.15	0.67	0.51
O/C molar ratio	0.03	0.03	0.23
Empherical formula	$CH_{1.149}N_{0.0599}S_{0.001}O_{0.032}$	$CH_{0.672}N_{0.061}S_{0.0008}O_{0.0299}$	$CH_{0.5106}N_{0.054}S_{0.0031}O_{0.233}$
Calorific value	27.6	29.1	26

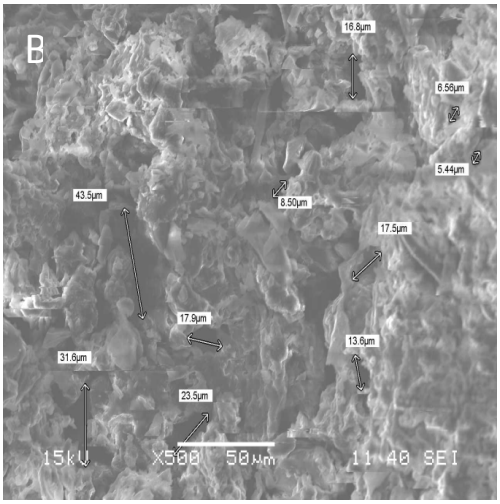
4.3.7 SEM ANALYSIS:

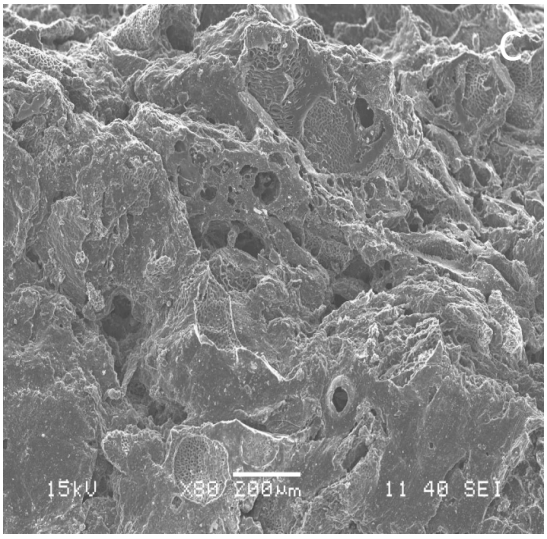
SEM-EDX is not only used for high magnification imaging but also for making a quantitative chemical analysis of unknown materials. The SEM can automatically perform analysis down to a particle size of 2 μm with the advantage of chemical characterization using EDX. With SEM in combination of EDX it is also possible to find out elemental composition of materials.-Scanning electron microscopy images were taken by using JEOL (JSM-6480 LV)

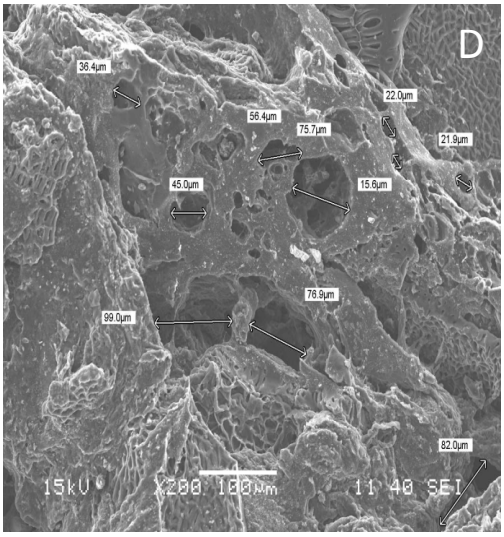
microscope having an acceleration voltage of 15 kV, equipped with a 6587 EDX scanning spectrometry detector.

SEM analysis was done to find the surface morphology of char and are shown in Figure 14(a,b,c,d,e,f). Image (a,b) are of neem char taken at 80X and 500X magnification. These images showed heterogeneous distribution of pores and rough texture. The average pore sizes present on the char surface of the char was found to be 18.4 µm.









Analysis with EDX of neem char surface shows the presence of C (60.95%), O (34.25%), as its major compositions. Images(c,d,e,f) are taken at 80X and 200X magnification for mustard and mahua char. The average pore size on the surface on mustard and mahua char was found to be 53 µm and 79.6 µm respectively. Presence of white color spots on surface shows the presence of residual ash. EDX analysis of mustard and mahua char showed the presence of

C(70.26%), O(18.33%) for mustard char and C(74.78%), O(157%) for mahua char.Table.22 shows the results of EDX analysis. Figure.15 shows the EDX spectra of neem, mustard and mahua char.

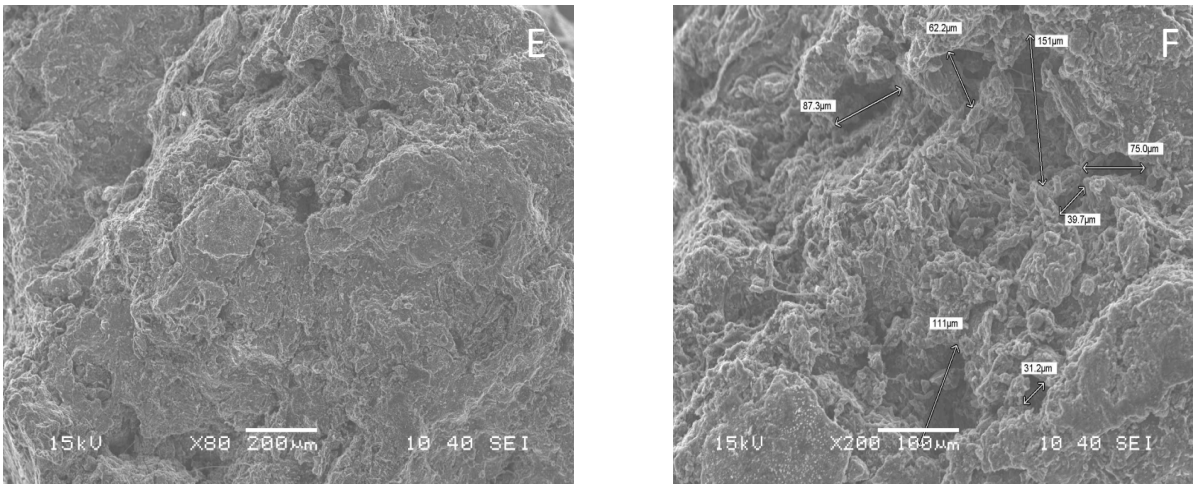


Figure. 14(a,b,c,d,e,f) SEM images of neem, mustard and mahua char taken at 80X, 200X and 500X magnification.

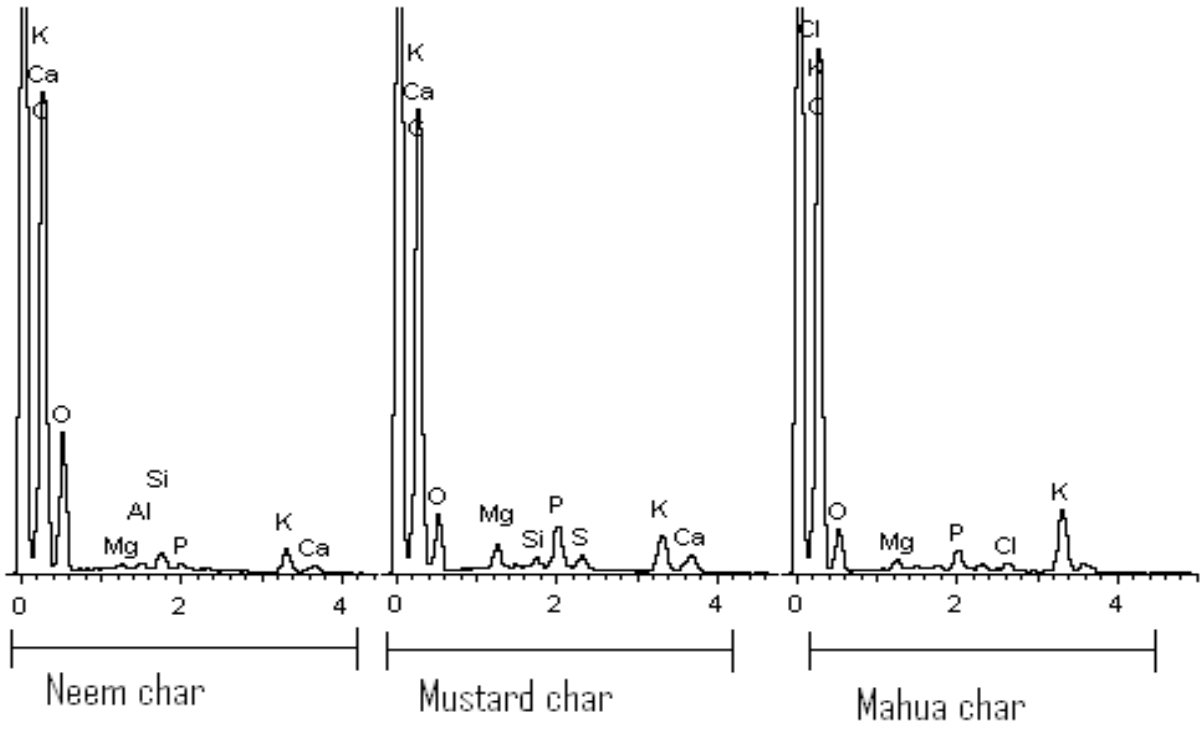


Figure. 15 EDX spectra of neem, mustard and mahua char

Table.22 Results of EDX analysis of neem, mustard and mahua char.

Element	Neem char	Mustard char	Mahua char
	Weight %		
C	60.95	70.26	74.78
O	34.25	18.33	15.7
Mg	0.25	1.22	0.55
P	0.35	2.87	1.42
S	--	1.07	---
Cl	--	--	0.73
K	2.38	4	6.83
Al	0.32	--	--
Si	0.88	0.53	--
Ca	0.63	1.73	--

CHAPTER - 5

ENGINE PERFORMANCE

5.1 COMBUSTION CHARACTERISTICS:

5.1.1 Cylinder Peak pressure:

The variation of cylinder peak pressure with brake power for different blends of mustard cake pyrolytic oil and diesel are given in Fig.16. The peak pressure depends on the amount of fuel taking part in the uncontrolled phase of combustion, which is governed by ignition delay. It is a measure of the amount of fuel accumulated during the ignition delay that takes part in the premixed combustion phase. Longer ignition delay is the reason for higher peak pressure. Cylinder peak pressure for all the blends was found to be lower than the diesel. The cylinder peak pressure for diesel increased from 54.9 bar at no load to 75.7 bar at full load. For a 30% blend of MCPO, peak pressure was found to be minimum which increased from 53.1 bar to 71.1 bar from no lad to full lad condition and the results are tabulated in Table.23.

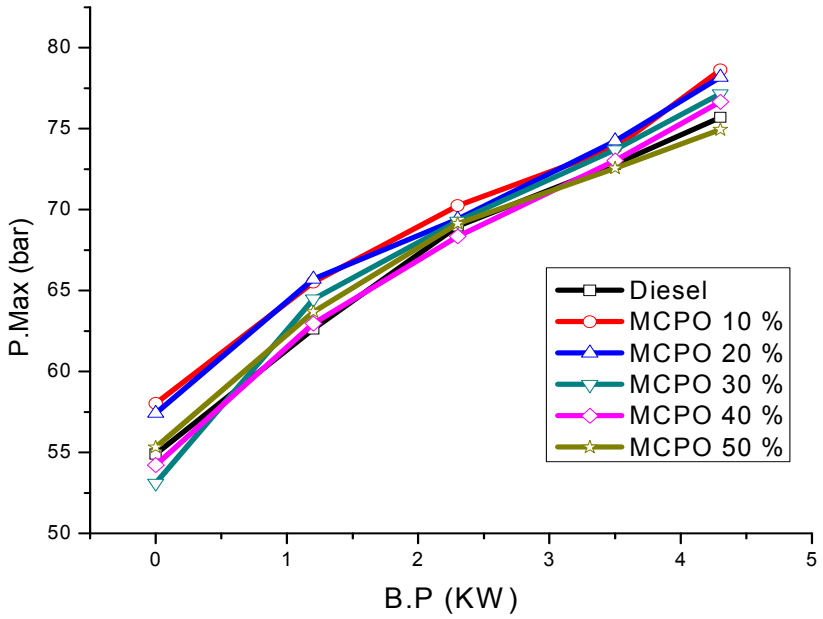


Figure.16 Variation of cylinder peak pressure with brake power

5.1.2 Combustion Pressure:

The variations of pressure at full load conditions with crank angle are given in Figure.17. From the graph it is clear that except for 10% blend peak pressures of all the other blends are almost equal to diesel which is 75.4 bar. The maximum peak cylinder pressure was 78.6 bar at 50% blend which is 3.82% more than diesel. Longer ignition delay at high load range increases the pressure.

Table. 23 Results of variation of maximum pressure with break power

Maximum Pressure(bar)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	54.91	58.02	57.42	53.11	59.23	55.32
1.2	62.62	65.52	65.72	64.48	62.96	63.68
2.3	68.99	70.24	69.42	69.29	68.35	69.12
3.5	72.81	73.82	74.24	73.7	71.03	72.56
4.3	75.70	78.63	78.19	77.16	76.65	74.94

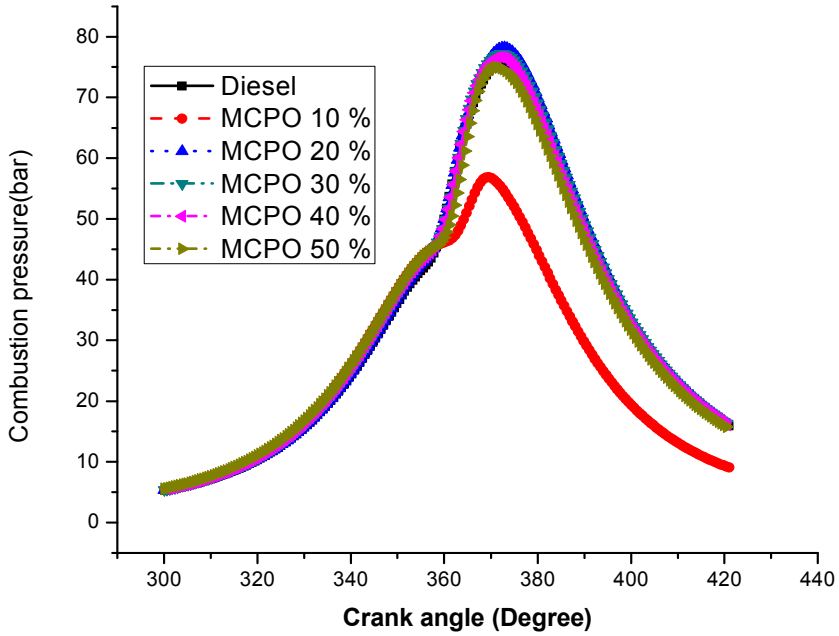


Figure.17 Variation of combustion pressure with crank angle

5.1.3 Maximum heat release rate:

The heat release analysis for different blends of mustard cake pyrolytic oil with diesel is given in Figure .18. The rate of heat release rate for 10%, 20%, 30% blends are 37.04, 56.26, 58.2, 57.6, 64.7 J/^{0}CA which are almost equal to that of diesel that is 52.01 J/^{0}CA. But for 50% blends the heat release rate was found to be 64.7 J/^{0}CA. which is about 24.3% higher than that of diesel. Increase in heat release rate at 40% and 50% blends could be due increased accumulation of fuel during the relatively longer ignition delay period resulted in higher rate of heat release while running with diesel. Poor atomization of fuel due increase in

viscosity with the increase in % of MCPO in diesel might have resulted in higher ignition delay resulting in more heat release.

5.1.4 Ignition delay:

Fig. 19 shows the variation of ignition delay with change in break power at different loads. Ignition delay is the time difference in the crank angle between the start of the injection and ignition of CI engines. It is clear that ignition delay decreased with increase in load and is slightly higher than that of diesel. For 40% and 50% blends of MCPO ignition delay was found to be higher and at no load and full load conditions. A maximum of 17 % increase was observed at break power of 4.3 KW the results are tabulated in Table.24.

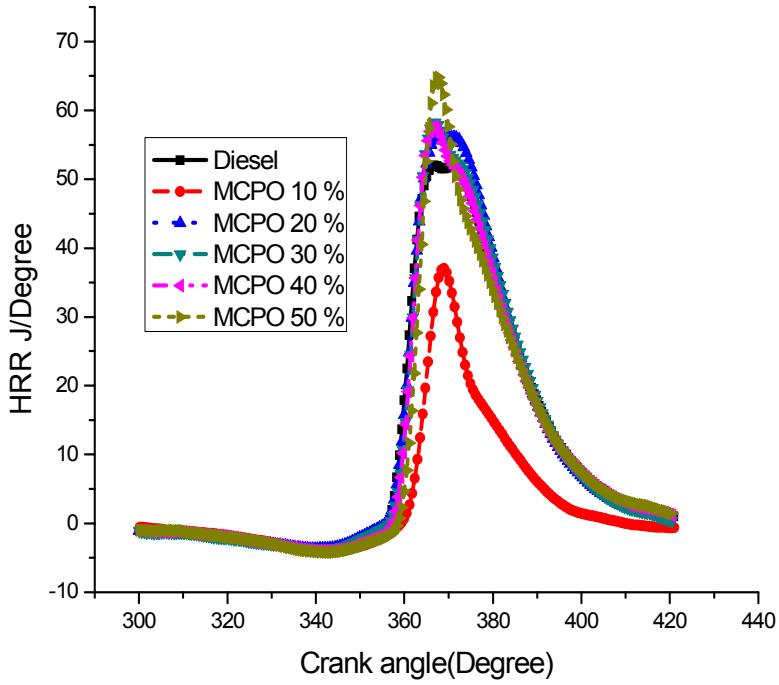


Figure.18 Variation of heat release rate with crank angle

The increase in ignition delay could be due to higher viscosities of fuel resulting in poor atomization with increase in % blends. MCPO has carbon compounds ranging form C_8 - C_{47} and the temperature inside the cylinder is not enough for the breakdown of these molecules resulting in higher ignition delay.

Table. 24 Results of variation of ignition delay with break power

Ignition delay (Deg. crank angle)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	17.0	15.2	16.1	18.5	20.1	21.4
1.2	14.3	13.34	14.1	14.6	16	18.1
2.3	13.0	12.7	12.7	13.2	15	16.4
3.5	13.0	12.7	13.3	13.6	14.4	16.2
4.3	12.7	12.1	13.2	13.5	13.5	14.9

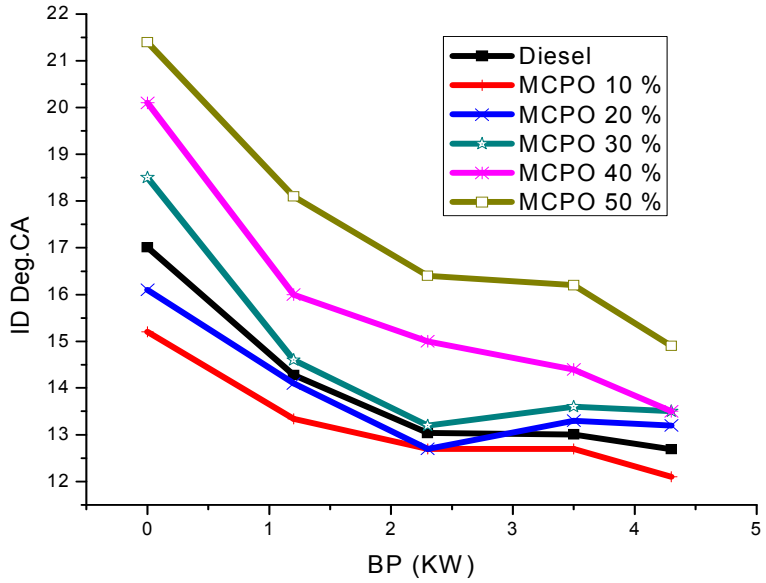


Figure.19 Variation of ignition delay with brake power

5.2 PERFORMANCE CHARACTERSTICS:

5.2.1 Break Thermal Efficiency (BTE):

Figure. 20 illustrate the variation of brake thermal efficiency with break power. BTE increased with increase in break power. It is clear except for 10% blend, all other blend of mustard cake pyrolytic oil showed a maximum efficiency at full load when compared to that of diesel. BTE of diesel at full load is 30.4% whereas for 10%, 20%, 30%, 40% and 50% blends brake thermal efficiency was found to be 29.56, 31.22, 31.77, 31.89 and 31.82. Increase in BTE of fuels blends could be due to the presence of more oxygenated compounds

which improved combustion characteristic resulting in more BTE the results of variation of BTE with BP are tabulated in Table.25.

Table. 25 Results of variation of break thermal efficiency with break power

Break Thermal Efficiency (%)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	0	0	0	0	0	0
1.2	17.14	19.24	18.15	18.14	18.39	18.54
2.3	26.10	26.34	26.87	27.07	28.26	27.96
3.5	30.02	30.51	30.77	31.15	32.48	31.86
4.3	30.47	29.56	31.22	31.77	31.89	31.82

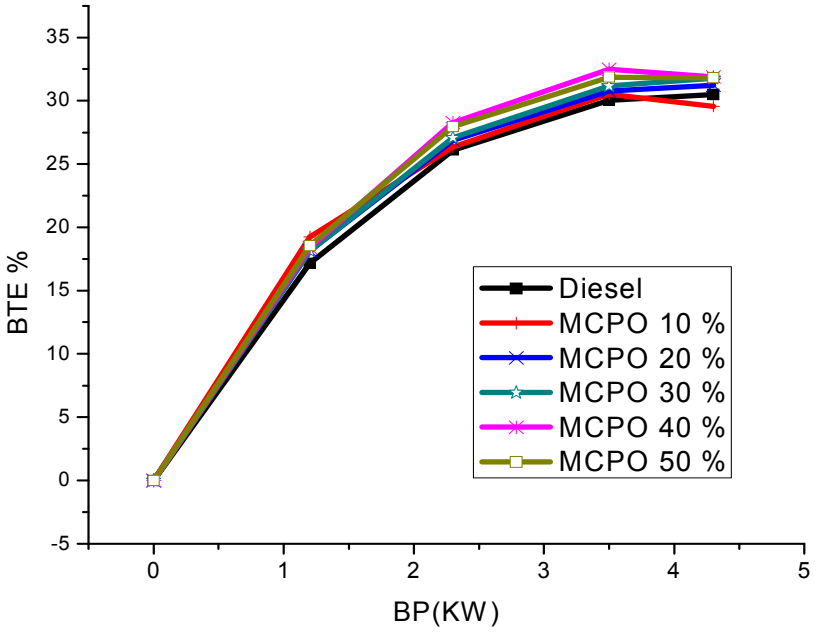


Figure.20 Variation of break thermal efficiency with brake power

5.2.2 Exhaust Gas Temperature (EGT):

Figure. 21 show the effect of BP on EGT for different blends of mustard cake pyrolytic oil. EGT increased with increase in BP. For diesel of EGT increased from 118 ^{0}C at no load to 270 ^{0}C at full load condition. EGT increased from 115 ^{0}C to 345 ^{0}C at no load to full load condition for 50% blend and the results are tabulated in Table.26. It was observed that with increase in blends of mustard cake pyrolytic oil in diesel, ignition delay increased resulting in

a delayed combustion and higher exhaust gas temperature or due to high heat release rates at higher blends and the increase in EGT is about 27.7 %.

Table.26 Results of variation of exhaust gas temperature with break power

Exhaust Gas Temperature (^{0}C)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	118	110	120	110	120	115
1.2	145	140	155	140	150	150
2.3	182	175	180	170	190	190
3.5	224	230	230	240	255	265
4.3	270	290	310	320	330	345

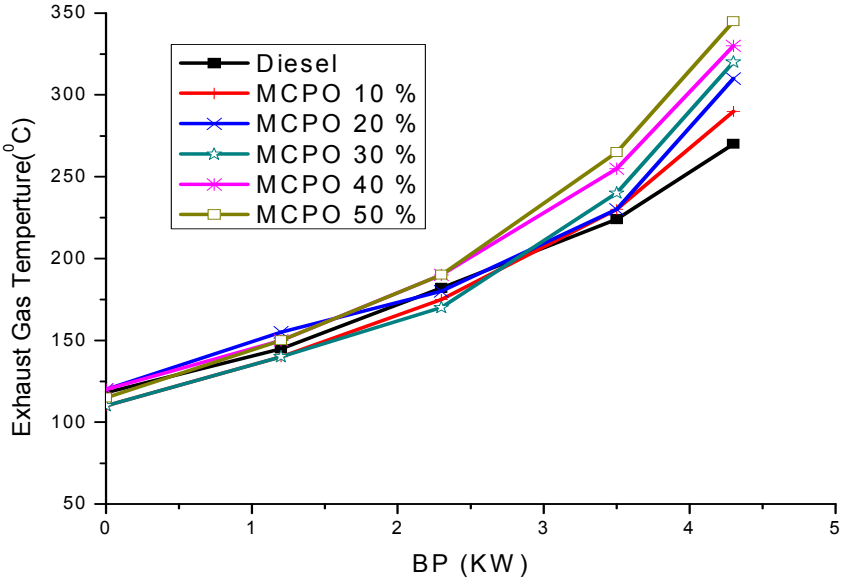


Figure.21 Variation of exhaust gas temperature with brake power

5.2.3 SPECIFIC FUEL CONSUMPTION:

Figure.22 illustrates the variation of the brake specific fuel consumption of diesel and various blends of mustard cake pyrolytic oil with break power. It was found that except for 40% and 50% blends, the specific fuel consumption for rest of the blends (10%, 20%, 30%) is close to diesel. This is due to the lower calorific values of the blends than diesel fuel, resulting in more requirement of fuel for constant power output and a maximum of 20% increase in fuel consumption was observed and the results are tabulated in Table.27.

Table. 27 Results of variation of specific fuel consumption with break power

Specific Fuel Consumption(Kg/KWHr)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	0	0	0	0	0	0
1.2	0.48	0.456	0.5	0.53	0.55	0.58
2.3	0.31	0.33	0.34	0.36	0.36	0.39
3.5	0.27	0.28	0.3	0.31	0.31	0.34
4.3	0.27	0.29	0.29	0.3	0.32	0.34

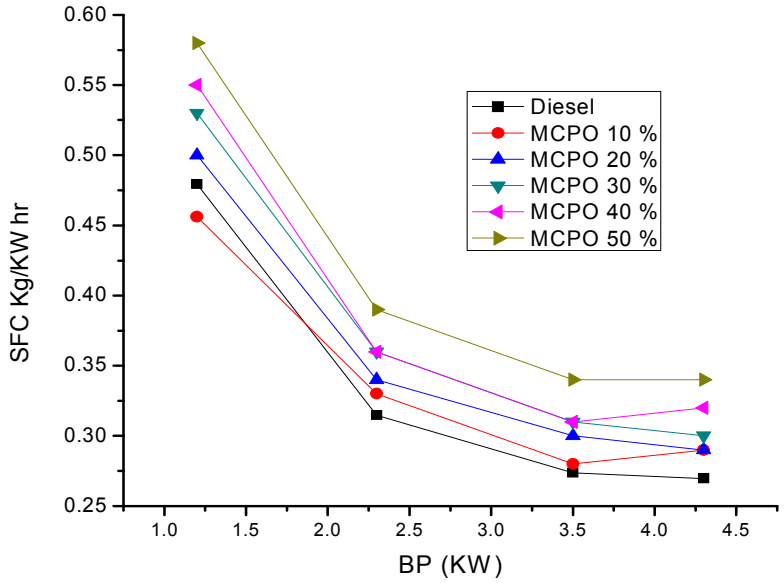


Figure.22 Variation of specific fuel consumption with brake power

5.3 EMISSION CHARACTRESTICS:

5.3.1 CO EMISSIONS:

CO emissions are produced because of the improper combustion of hydrocarbons. These emissions mainly depend on air to fuel ratio and engine temperature. The variation of CO emissions with break power (BP) for different blends of mustard cake pyrolytic oil is shown in Figure. 23 and are compared with diesel. It was observed that CO emissions decreased initially with increase in load and then increased sharply and the results are tabulated in Table.28. The decrease in CO emissions initially could be due to lower cylinder temperatures

that might have increased with increase in load due to the accumulation of more fuel inside the cylinder. Because of more smoke formation by the excess supply of fuel on further increase in loads might have prevented the oxidation of CO to CO_2 resulting in increase of CO emissions sharply. The minimum and maximum CO produced was 0.01– 0.03 %.

5.3.2 HC EMISSIONS:

Figure. 24 shows the HC emissions for different blends of mustard cake pyrolytic oil and are compared with diesel. For a 30% and 40% blends, HC emissions are found to be lower than diesel emissions. They also follow a similar trend of CO emissions and these emissions initially decrease and then increased with increase in break horse power (BHP). The minimum and maximum HC produced was 8 and 24 ppm resp. The increase in the HC could be due to poor atomization of the fuel or due to higher viscosities at higher blends and the results are tabulated in Table.29.

Table. 28 Results of variation of CO emissions with break power

CO Emissions (% vol)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	0.02	0.02	0.02	0.02	0.02	0.02
1.2	0.015	0.02	0.017	0.013	0.019	0.02
2.3	0.01	0.01	0.01	0.01	0.01	0.01
3.5	0.01	0.01	0.01	0.01	0.01	0.01
4.3	0.01	0.02	0.02	0.01	0.02	0.03

Table. 29 Results of variation of HC emissions with break power

Hydrocarbon Emissions(ppm)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	22	24	23	18	22	24
1.2	15	19	17	11	15	21
2.3	11	15	13	7	11	17
3.5	11	15	14	8	12	16
4.3	14	20	17	13	15	22

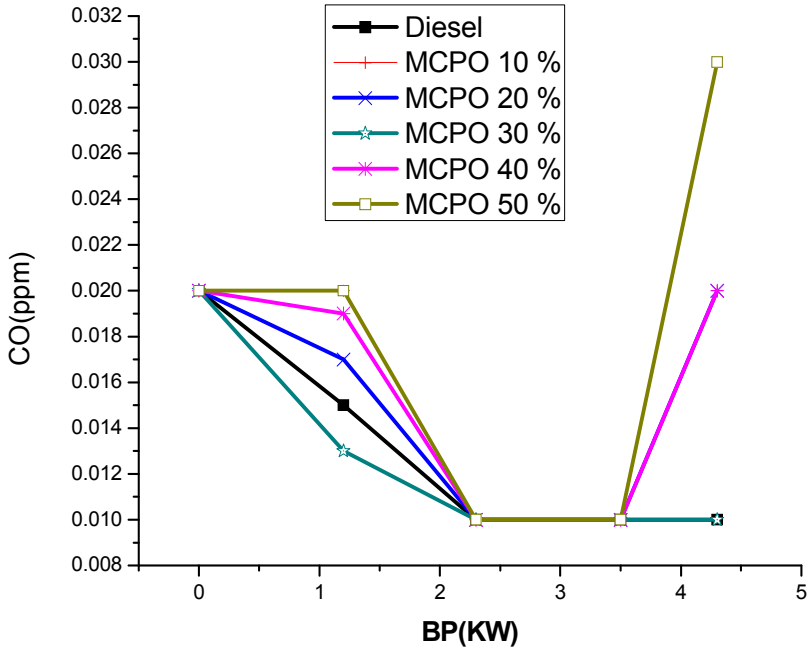


Figure.23 Variation of CO emissions with brake power

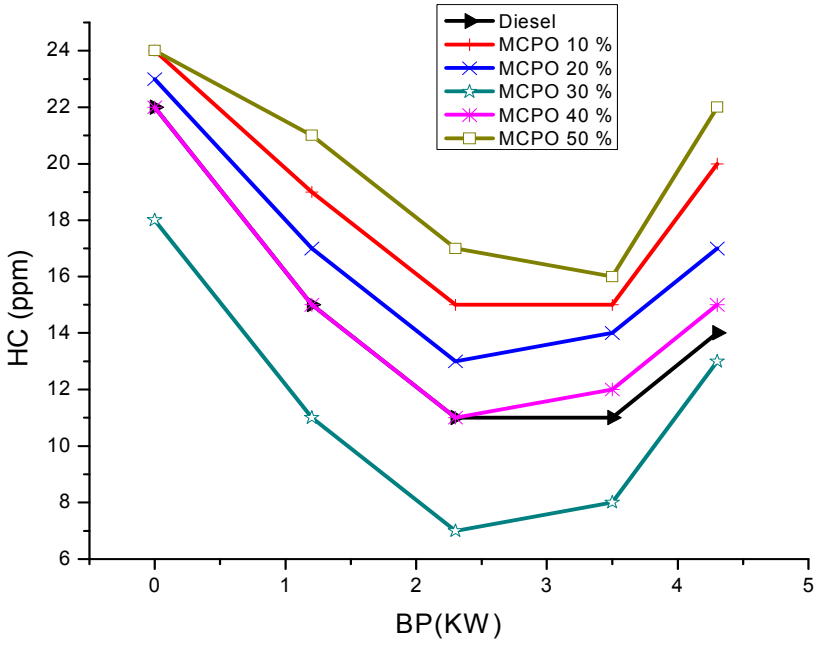


Figure.24 Variation of HC emissions with brake power

5.3.3 CO_2 EMISSIONS:

The emission levels of CO_2 for various blends of mustard cake pyrolytic oil and diesel is shown in Figure. 25. It can be observed that the CO_2 initially decreased and later increased. The minimum and maximum CO_2 produced was 1% at 1.2 BP and 2.7 % at 4.3 break power. The increase in trend of CO_2 emission with increase in load is due to the higher fuel entry. Generally biofuels contain lower carbon content as compared to diesel and hence the CO_2 emissions are comparatively lower and the results are tabulated in table.1.

Table. 30 Results of variation of CO_2 emissions with break power

CO_2(% vol)						
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	1.33	1.2	1.3	1.2	1.2	1.3
1.2	1.16	1.1	1.2	1	1.1	1.2
2.3	1.2	1.2	1.3	1.1	1.2	1.4
3.5	1.6	1.8	2	1.7	1.9	2.1
4.3	2.6	2.4	2.5	2.5	2.6	2.7

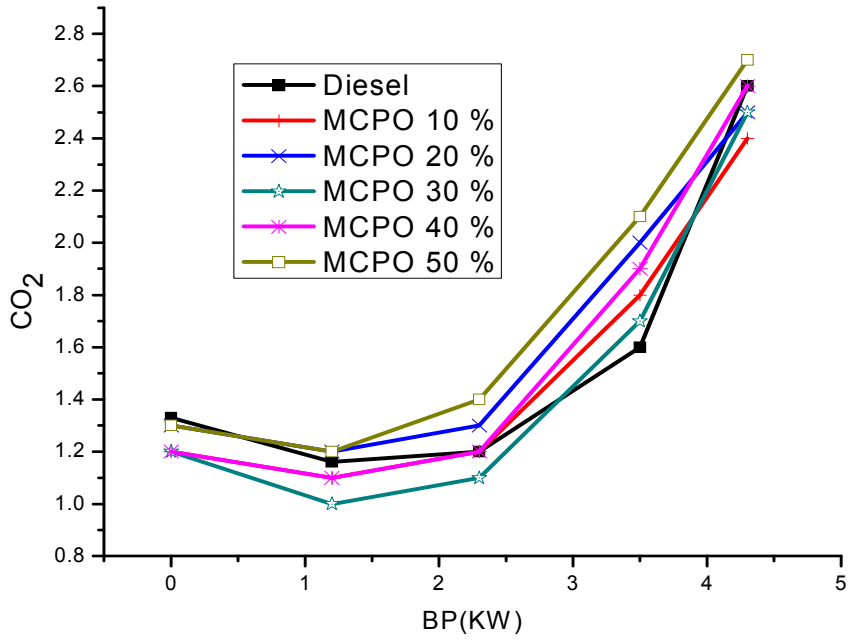


Figure.25 Variation of CO_2 emissions with brake power

5.3.4 NO EMISSIONS:

The NO emissions as parts per million (ppm) for different blends of mustard cake pyrolytic oil and diesel are given in Figure. 26. It is very clear that NO emissions increased gradually with increase in break power and are very much less when compared to diesel. For 30% blend NO emissions was found to be minimum, which is about 106 ppm to 417 ppm from no load to full load condition when compared with diesel it is 115 ppm to 502 ppm and the results are tabulated in Table.31.

Table. 31 Results of variation of NO emissions with break power

	NO(ppm)					
BP(KW)	Diesel	10%	20%	30%	40%	50%
0	115	104	114	106	90	80
1.2	158	168	175	124	127	142
2.3	233	209	204	193	182	198
3.5	353	362	385	301	348	316
4.3	502	449	457	417	438	445

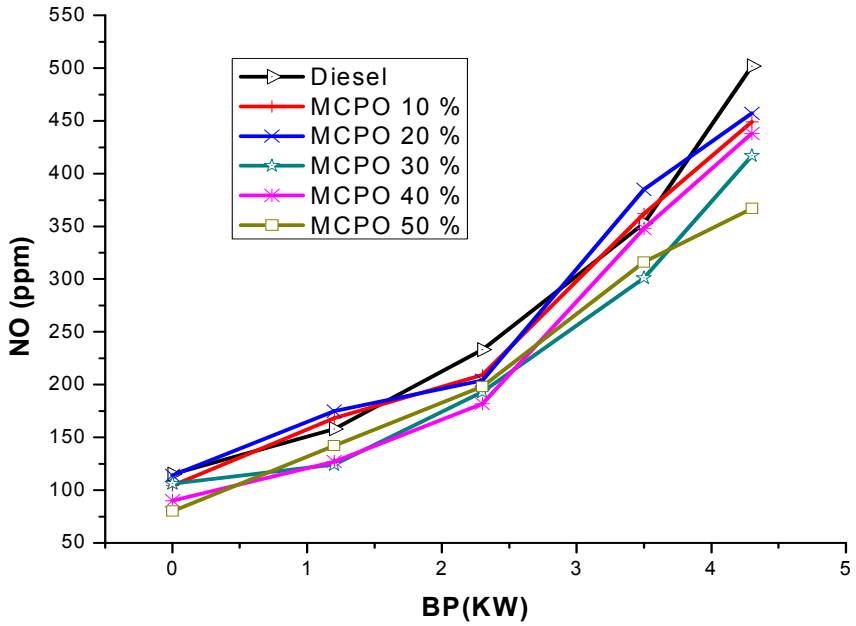


Figure.26 Variation of NO emissions with brake power

NO emissions decreased by 11% along with increase in break power when compared to diesel. Increase in NO emissions could be either due to the fact that vegetable based fuels have little nitrogen content in the form of amides and nitriles or with increase in load, the overall fuel-air ratio increases resulting in an increase in the average gas temperature in the combustion chamber resulting in increase of NO formation, which is sensitive to temperature increase.

CHAPTER - 6

CONCLUSION

In this study, an agricultural by-product neem, mustard and mahua cake was taken as a biomass sample and pyrolysis experiments was done in a semi batch reactor under different temperatures of 350-700 ^{0}C to obtain maximum yield of bio-oil. The following conclusions drawn from the present work:

- The maximum bio-oil yield was 40.2% at an optimum temperature of 400 ^{0}C for neem cake, 53.2% for mustard cake and 41.3% for mahua cake at a temperature of 550 ^{0}C .
- Char yield decreased with increase in temperature, the gaseous yield decreased initially, became optimum at the point where there is maximum yield of liquid product and then increased.
- Reaction time decreased with increase in temperature.

This shows that temperature has significant effect on pyrolysis yields, reaction time and conversion efficiencies.

- FTIR analysis showed that the bio-oils compositions were dominated by oxygen and nitro group due to the presence of carboxylic and amines apart from the presence of straight chain alkanes and alkenes.
- 1H NMR analysis of bio-oil proves that β- CH_3, CH_2 hydrogen protons are attached to an aromatic ring in higher proportions.
- GC-MS analysis showed the presence of about 35 chemical compounds in the bio –oil of different carbon molecules. Separation and analysis of these materials may lead to major industrial applications.
- Presence of pores shown by SEM-EDX analysis paves a path for using this char as an adsorbent.

Chemical characterization of the bio-oil showed that, it can be utilized as either synthetic fuels or a source of chemical feedstock.

Following conclusions were drawn from Engine performance:

- There was a 6% increase in maximum pressure in the cylinder when compared with diesel at full load condition having a break power 4.3KW for 30% blend.
- Variations of rate of heat release with crank angle showed that with increase in % blends there was a significant increases and it accounts to 12% when compared to diesel for 30% blend

- There was a 11% increase in specific fuel consumption with increase in break power due to low calorific value of the fuel
- For a 30% blend there was a 4% increase in break thermal efficiency.
- CO emissions initially decreased and then increased with increase break power and for 30% blend these emissions are almost same when compared to diesel.
- HC emissions initially decreased and then increased with increase break power and for 30% blend these was 36% reduction at 2.3 KW break power.
- CO_2 emissions increased gradually and at lower break powers they are less than diesel emissions, for 30% blend, these emissions decreased to 3%.
- NO emission increased with increase in break power but are less than emissions of diesel these emissions are 11% lesser than diesel

From the above, it can be concluded that 30% blend of mustard cake pyrolytic oil with diesel can be substituted with diesel.

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